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ON SOME REGULARITIES OF THE RELATIVE ATOMIC ABUNDANCE OF THE PRINCIPAL ISOTOPES AND ISOBARS

E. P. Ozhigov

In one of our communications [1] it was shown that the distribution of isotopes of the highest percentage content in the pleiads is a function of three forms of nuclear periodicity [2]: the periodicity associated with the even and odd atomic numbers of the elements, the nuclear periodicity of the Mendeleev type, and finally, the periodicity causing at the end of the periodic system the displacement of the isotopes of highest percentage content in the direction of higher mass numbers.

The last form of periodicity was considered by S. A. Shchukarev [2] in connection with the observation of the intersection of the artiad and perissad curves; it was also investigated by A. P. Znoiko [3, 4] in the form of the specific charge of the nucleus which keeps constant the ratio between the number of protons and neutrons in the principal isotope.

It appeared of interest to pass from the isotopes of highest percentage content to the isotopes of highest atomic distribution, since the atomic percent more clearly characterizes the stability of the nuclear structure of the elements.

The necessary data for calculation of the atomic abundance of isotopes and isobars of the stable elements and of the period of half decay of the isotopes of the radioactive elements in the range of mass numbers from 1 to 245 are taken from tables (literature data [5-7]).

In Table 1 is given the distribution of the principal isotopes in the periodic system of D. I. Mendeleev which possess either the highest atomic abundance or the maximum life period.

The effect of the forms of nuclear periodicity that we enumerated above is shown in the distribution of isotopes and isobars according to atomic abundance. The periodicity of the elements according to even or odd atomic number, is manifested as a rule in less wide distribution of isotopes with odd atomic number, but the number of isotopes of these elements does not exceed 2. This result is not new to science but supplements the data for the radioactive elements. On transition to the region of the unstable portion of the periodic system, the ratios between the radioactive isotopes remain the same as in the stable elements of even and odd atomic numbers. The number of radioactive isotopes of odd atomic numbers in the pleiads does not exceed 2, but the number of radioactive isotopes of even atomic numbers varies within wider limits and can also be very large.

Nuclear periodicity of the Mendeleev type is manifested in the coincidence of the series of isotopes according to atomic abundance with the nodal points of the periodic system of the pleiads of isotopes which was proposed by us [1]. If we ignore the rare isotope of lithium with mass 5, then the principal isotopes and isobars will, in order of atomic abundance, occupy the following number of places along the periods: 4, 16, 16, 45, 48, 88.

These data enable us to conclude that the natural periodic system of the pleiads of isotopes is characterized by a deep inner symmetry which is reflected in a constant measurement of the system in units of atomic weight in the vertical and horizontal directions.

We may also note that the simple empirical law that those even elements predominate in the earth's crust (as well as on the earth in general and in meteorites) whose atomic numbers differ by six or a multiple of six [7] is associated in some fashion with nuclear periodicity of the Mendeleev type.

The largest number of isotopes in order of atomic abundance occurs in Groups II and IV; the number is smaller in VI and still smaller in Group VII. Of the elements of even atomic number, the zero group is poor in isotopes, while among the elements of odd atomic numbers Group VII is poor in isotopes. The maxima in respect of abundance through 6 and 12 numbers are exhibited primarily by Group II (calcium, strontium, barium), followed by Group IV (silicon, tin), Group VI (oxygen) and finally by VIII (iron).

TABLE 1

Distribution of isotopes and isobars of highest atom percent in Mendeleev's periodic system

Periods	Groups I	II	III	IV	V	VI	VII	0			
1							1H 1, 2	2He 3, 4			
2	3Li 5, 6, 7	4Be 9	5B 10, 11	6C 12, 13	7N 14, 15	● 8O 16, 17, 18	9F 19	10Ne 20, 21, 22			
3	11Na 23	12Mg 24, 25, 26	13Al 27	● 14Si 28, 29, 30	15P 31	16S 32, 33, 34	17Cl 35, 37	18Ar 36, 38			
4	19K 39, 41*	● 20Ca 40, 42, 43, 44	21Sc 45	22Ti 46, 47, 48, 49, 50	23V 51	24Cr 52, 53	25Mn 55		● 26Fe 54, 56, 57, 58	27Co 59	28Ni 60, 61, 62
	29Cu 63, 65	30Zn 64, 66, 67, 68	31Ga 69, 71	32Ge 70, 72, 73, 74, 76	33As 75	34Se 77, 78, 80, 82	35Br 79, 81	36Kr 83			
5	37Rb 85	● 38Sr 84, 86, 87, 88	39Y 89	40Zr 90, 91, 92	41Nb 93	42Mo 94, 95, 96, 97, 98	43Tc –		44Ru 99, 100, 101, 102	45Rh 103	46Pd 104, 105
	47Ag 107, 109	48Cd 106, 108, 110, 111, 113, 114	49In 115*	● 50Sn 112, 118, 119, 120, 122, 124*	51Sb 121, 123	52Te 125, 126, 128, 130	53I 127	54Xe 129, 131			
6	55Cs 133	● 56Ba 132, 134, 136, 137, 138	57La 139	72Hf 177, 178, 179, 180	73Ta 181	74W 182, 183, 184	75Re 185, 187*		76Os 186, 188, 189, 190, 192	77Ir 191, 193	78Pt 194, 195, 196
		58Ce 140	59Pr 141	60Nd 142, 143, 144, 145, 146, 148, 150	61Pm –	62Sm 147*, 149, 152, 154	63Eu 151, 153	64Gd 155, 156, 157, 158, 160			
		65Tb 156	66Dy 161, 162, 163, 164	67Ho 165	68Er 166, 167, 168, 170	69Tu 169	70Yb 171, 172, 173, 174, 176	71Lu 175			
7	79Au 197	80Hg 198, 199, 200, 201, 202	81Tl 203, 205	82Pb 206, 207, 208	83Bi 209	84Po 210*, 211*, 213*, 214*, 215*, 216*	85At 217*, 218*	86Rn 212*, 219*, 220*, 222*			
	87Fr 221*	88Ra 223*, 224*, 225*, 226*, 228*	89Ac 227*	90Th 229*, 230*, 232*	91Pa 231*	92U 233*, 234*, 235*, 238*	93Np 297*	94Pu 236*, 239*, 240*, 242*	95Am 241*	96Cm 243*, 244*	
				97Bk	98Cf						

Notes

1. The predominant isotopes are underline
2. * – radioactive isotopes.
3. Black circles denote elements on which fall the maxima of abundance through 6 or 12 atomic numbers

TABLE 2

Element	O	Si	Ca	Fe	Sr	Sn	Ba
Atomic number	8	14	20	26	38	50	56
Difference between numbers	6	6	6	12	12	6	

The third form of nuclear periodicity is characterized by the most plentiful isotope being shifted from the start of the pleiad to the middle or the end of the pleiad of isotopes of the element (we have underlined the most plentiful isotopes).

Transfer of the principal isotope to the middle or the end of the pleiad corresponds in the majority of cases to a fall in the plentifulness of the elements.

This form of nuclear periodicity first appears exceptionally in the upper part of the table in the elements lithium, beryllium (allowing for the unfilled position 8) and boron, and evidently lowers their atomic abundance.

It is possible that under the influence of this form of nuclear periodicity the maximum of abundance through the six elements at germanium is not manifested, since, starting from the element gallium the principal isotope is shifted to the end of the pleiad, and this position is maintained, with rare exceptions, to the end of the periodic system.

SUMMARY

1. The data considered enable the conclusion to be drawn that the distribution of isotopes according to atomic percentages is also associated with the known types of nuclear periodicity which were previously discussed [1], includ- nuclear periodicity of the Mendeleev type.

2. When the isotopes and isobars of highest atomic abundance are arranged in series corresponding to the six periods of Mendeleev's periodic system, they occupy the following number of places on the scale of mass numbers: 4, 16, 16, 45, 48, 88. This series numerically coincides with the nodal points of the periodic system of the pleiads of isotopes proposed by us [1] and testifies to a profound inner symmetry of the system as a whole.

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INVESTIGATION OF THE UNSTABLE EQUILIBRIA BETWEEN LIQUID PHASES. IV.

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Results of investigations have previously been reported [1,2] of those ternary systems with unstable equilibrium between the liquid phases in which stable chemical compounds are not formed between the components. The present work is the next stage in the study of unstable equilibria between the liquid phases, and deals with the introduction into a binary homogeneous (both in the stable and unstable states) system of a third component leading to formation of stable chemical compounds. With this objective a study was made of the ternary system picric acid - salicylic acid - water.

EXPERIMENTAL

The ternary system picric acid - salicylic acid - water contains the following binary systems.

1. System picric acid - water. This was previously studied by the melting and layer-formation methods [3]. In it is observed a region of stable equilibrium between the liquid phases with an upper critical temperature of solution. In this system the upper critical point is not reached; the triple points contain 8.2 and 95.8% picric acid at a temperature of monotectic equilibrium of 104.8°.

2. System salicylic acid - water. This has also been studied by melting and layer formation [4]. It contains a region of unstable equilibrium between the liquid phases with an upper critical temperature of solution. The upper critical point corresponds to a composition containing 32% salicylic acid at a temperature of 89.1°; above it is a nearly horizontal portion of the curve of crystallization at 104°.

3. System picric acid - salicylic acid. This is homogeneous both in the stable and unstable states. As was shown by the investigations described below on layer formation, the components of this system form a picrate containing 6 molecules of salicylic acid to 1 molecule of picric acid, i.e., it contains 21.64% picric acid. This picrate of salicylic acid was stable in the liquid phase in the unstable state.

Consequently the ternary system under investigation contains two binary systems with layer formation (one of them unstable) and a third system with formation of a chemical compound which is stable in the unstable state.

As in the previous studies, the investigations were carried out in sealed ampoules in an oil thermostat by the polythermal method of Alekseev [5]. The following components were taken: picric acid recrystallized from alcohol with m.p. 122.5°; salicylic acid, chem. pure grade with m.p. 155°; twice-distilled water.

In the three-component system, picric acid - salicylic acid - water, a study was made of the polythermal sections through its prism, starting from the water edge on the side of the binary system picric acid - salicylic acid. In all, 8 such sections were investigated with a content of 7, 14, 19, 22, 25, 30, 40 and 50% picric acid. Sections containing more than 50% picric acid were not investigated. In all sections the equilibrium was studied between the liquid phases after preliminary experiments had shown that the equilibrium was metastable in all of them. Nevertheless, for ocular confirmation of this in sections containing 22 and 40% picric acid, the crystallization above the layer formation was studied. The numerical data for the polythermal sections are set forth in Table 1, and examples of the polytherms are plotted in Fig. 1.

As Fig. 1 shows, the polytherms of layer formation are unstable and consist of curves with flat maxima. These maxima fall from section to section from both sides with progressive approach of the sections to the composition of the picrate. The polytherms of layer formation located to the left of the composition of the picrate are sharply displaced towards the water corner; the polytherms more to the right of the picrate composition are more and more shifted to the middle of the section with increasing distance from the picrate composition. Above the curves of layer formation the polytherms of crystallization Kp have a nearly horizontal portion, similar to that in the binary system salicylic acid - water.

TABLE 1

Polytherms of the System Picric Acid - Salicylic Acid - Water

No. of section	Water (wt.-%)	Layer formation temp.	No. of section	Water (wt.-%)	Layer formation temp.	No. of section	Water (wt.-%)	Temperature of layer formation	Temperature of crystallization	No. of section	Water (wt.-%)	Temperature of layer formation	Temperature of crystallization
1 7% P.A.* 93% S.A.*	35.00	58.0°	5 25% P.K. 75% S.A.	35.00	61.0°	3 19% P.A. 81% S.A.	40.00	64.0°	–	7 40% P.A. 60% S.A.	30.00	70.0°	–
	40.32	68.5		40.03	68.0		50.00	69.0	–		37.00	79.0	–
	50.00	74.0		50.04	71.0		60.01	69.0	–		40.00	80.0	–
	60.00	76.5		60.31	71.0		70.00	69.0	–		50.00	83.0	–
	70.58	77.0		70.02	70.0		80.43	68.0	–		60.00	83.0	92.0°
	80.04	77.0		80.04	67.0		90.00	65.0	–		70.00	83.0	–
	90.33	74.0		90.00	61.0						80.00	75.0	93.0
	93.00	65.0									85.00	59.5	93.0
2 14% P. A. 86% S.A.	40.30	65.5	6 30% P.K. 70% S.A.	35.00	66.0	4 22% P. A. 78% S.A.	35.00	57.0	–	8 50% P. A. 50% S.A.	25.00	76.0	–
	50.00	70.0		40.61	70.0		40.43	63.0	–		30.00	89.0	–
	60.54	72.0		50.07	73.5		50.03	69.0	104°		40.00	97.0	–
	70.32	72.0		60.05	73.0		60.00	69.0	–		50.00	98.0	–
	80.03	71.0		70.00	71.5		70.07	69.0	99.0		60.00	97.0	–
	90.07	65.5		80.95	67.0		80.03	65.5	–		70.00	96.0	–
				95.00	53.0		90.00	60.0	99.0		80.00	85.0	–
											85.00	62.0	–

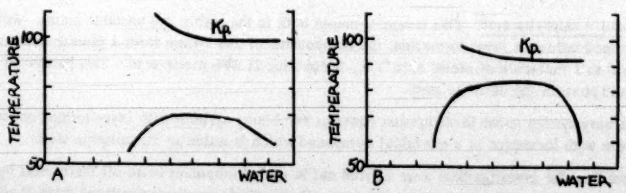

Fig. 1. Solubility polytherms of the system picric acid - salicylic acid - water.
A - mixture of 22% P. A. with 78% S. A.; B - mixture of 40% P. A. with 60% S. A., Kp - crystallization curve.

Through the critical point K_1 of the system salicylic acid - water and the maximum points of the sections can be drawn the critical line (Table 2, Fig. 2) whose projection on to the side of the system salicylic acid - picric acid is represented by curve K_1 GK, where K is the maximum of the last section with a content of 50% picric acid. The critical curve comprises two branches which intersect with falling temperature at point G lying in the section corresponding to the composition of the picrate and a content of 21.64% picric acid. This section is a quasi-binary section of the prism of the ternary system under examination. In this section point, G corresponds to the critical point of unstable layer formation of the system picrate - water; it lies at 68.5° and has the composition 61% water, 8.4% picric acid and 30.6% salicylic acid.

The projection of the critical line on to the triangle of composition is represented in Fig. 3 by curve K_1GK_2 which has an inflexion point at G in the quasi-binary section. In both projections of the critical line there is observed the interesting feature that the chemical compound of the binary system is reflected on the critical line of the layer formation region of the ternary system.

* P. A. is picric acid, S. A. is salicylic acid.

TABLE 2

Composition of points of the critical line

Temperature	Composition (weight - %)		
	Picric acid	Salicylic acid	Water
89.1°	0.0	32.0	68.0
77.0	2.1	27.9	70.0
72.0	4.9	30.1	65.0
69.0	7.2	30.8	62.0
68.5	8.4	30.6	61.0
69.0	8.8	31.2	60.0
71.0	11.3	33.7	55.0
73.5	14.1	32.9	53.0
83.0	19.6	29.4	51.0
98.0	25.0	25.0	50.0

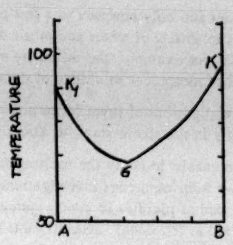

Fig. 2. Projection of the critical line onto the side of the binary system salicylic acid - picric acid. A – mixture of water and S. A., B – mixture of water and 50% mixture of P. A. and S. A. Explanation in text.

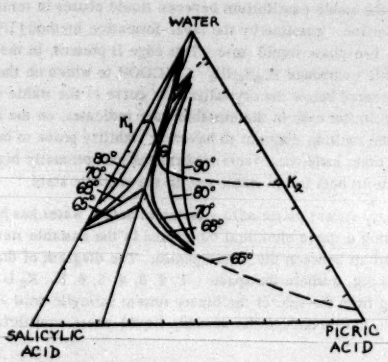

Fig. 3. Solubility isotherms of the ternary system picric acid - salicylic acid - water
Top corner: water. Left: salicylic acid. Right: picric acid

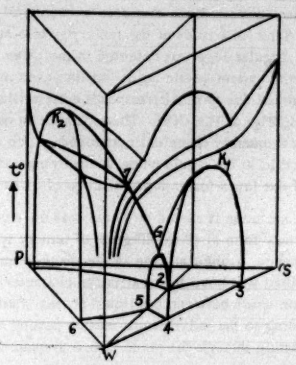

Fig. 4. Temperature-concentration prism of the ternary system picric acid (P) - salicylic acid (S) - water (W).

On the basis of the obtained polythermals of layer formation plots were prepared of the isothermal sections of the prism of the ternary system picric acid - salicylic acid - water. In all 5 isotherms were plotted at 65, 68, 70, 80 and 90°, the projection of which onto the triangle of composition is represented in Fig. 3. This diagram shows that at high temperatures (70, 80 and 90°) in the unstable state the isotherms of layer formation deviate from the solubility sections of the corresponding binary systems and are located inside the prism of the ternary system in the form of two separate binodal curves. At 68.5° these curves touch one another in the quasi-binary section of the ternary system, and at lower temperatures they run together to form a singular synclinal edge corresponding to the composition of the picrate. Consequently in this ternary system on the unstable portion of the whole space of equilibrium between the liquid phases, we have a singular synclinal edge corresponding in the binary system picric acid - salicylic acid to the composition in which the ratio of the components of the binary system is 1 : 6. This is evidence that in the binary system, picric acid - salicylic acid, there is formed a chemical compound of the indicated composition which is stable in the liquid phase in the unstable state.

The presence in this ternary system of a singular fold of the synclinal type is accounted for by the specific character of the solubility in the system. The reciprocal solubility of the liquids in the unstable state, starting from that in the binary system salicylic acid - water, gradually increases in the sections with increasing picric acid content and attains a maximum in the quasi-binary section. With further increase of picric acid content in the sections, the solubility

in them declines and only amounts to a few percent on reaching the binary system picric acid - water. Consequently, the reciprocal solubility of water and picric acid is considerably greater than that of water and salicylic and picric acids. Actually, at 68° for example, the solubility of water in salicylic acid is 34%, in picric acid 4%, and in their picrate 48%. This character of reciprocal solubility of the components of the system accounts for the synclinal type of singular fold.

Thus investigations of layer formation can establish the existence of chemical compounds in binary homogeneous systems not only in the stable state, as already shown [6,7] but also in the unstable state.

We were unable to apply the melting technique to the study of the binary system, picric acid - salicylic acid; however it is known from numerous investigations [8] that on the melting diagrams curves with a flat maximum (distectics) usually correspond to picrates in binary systems. Consequently binary systems which form picrates (even with amines) must be regarded as irrational systems; this must be particularly true of the system now under consideration in which a picrate of an acid is formed. Nevertheless, notwithstanding even the presence in the mixtures of a polar solvent (water) a singular element was formed in the ternary system at the surface of equilibrium between the liquid phases. Similar cases in physicochemical analysis have been previously encountered in a study of systems by highly sensitive methods, for example by viscosity measurements. Thus in the binary system tin bromide - ethyl acetate [9], 2 compounds were detected from the melting diagram: one melting without decomposition with the composition $SnBr_4 \cdot CH_3COOC_2H_5$, and the other melting with decomposition with the composition $SnBr_4 \cdot 2CH_3COOC_2H_5$. The viscosity isotherm at −5° contains a sharp maximum corresponding to a composition almost identical with that of the compound melting with decomposition. Moreover, analogous cases have also been encountered in a study of the stable equilibrium between liquid phases in ternary systems. Thus, in a study of the ternary system, acetic acid - aniline - gasoline, by the layer-formation method [10], a synclinal singular edge was detected in the space of the stable, two-phase liquid state. This edge is present, in the binary irrational system, acetic acid - aniline, even up to the unstable compound $2C_6H_5NH_2 \cdot CH_3COOH$ to which on the melting diagram of this system corresponds a crystallization curve located below the crystallization curve of the stable compound $C_6H_5NH_2 \cdot 2CH_3COOH$. The existence in our system of a similar case in the unstable state indicates, on the one hand, that frequently chemical compounds which appear from the melting diagram to have low stability prove to be adequately stable in the liquid phase at low temperatures. On the other hand these facts confirm the exceptionally high sensitivity of the layer-formation technique of investigation of systems both in the stable and in the unstable state.

In conclusion it should be noted that the study of the ternary system, picric acid - salicylic acid - water, has brought to light a new form of phase diagram of ternary systems containing a stable chemical compound in the unstable state, and in consequence, a singular edge in the space of unstable equilibrium between the liquid phases. The diagram of the system described will have the qualitative character represented in Fig. 4 where the space 1, 2, 3, 4, 5, 6, K_1, K_2 is the equilibrium space between the liquid phases. Part of it, starting from the side of the binary system salicylic acid - water and extending to the polythermic section passing through point 7, corresponds to the unstable liquid-phase equilibria. The section passing through the plane 2, 5, G is quasi-binary.

SUMMARY

1. A study was made of the solid and liquid phases in the three-component system, picric acid - salicylic acid - water. A new form of equilibrium diagram was revealed with a synclinal singular edge in the space of the unstable two-phase liquid state.

2. Layer formation investigations of this ternary system revealed the existence in the binary system, picric acid - salicylic acid, of a chemical compound which is stable in the unstable state and with a picric acid / salicylic acid ratio of 1 : 6.

3. It was shown to be entirely possible to study binary homogeneous systems by the method of investigation of them in ternary systems by observing the layer formation in the unstable state.

4. It was found that formation of a chemical compound in the binary system, picric acid - salicylic acid, is reflected on the critical line of the space of the two-phase liquid equilibrium of the ternary system.

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THE SOLID-PHASE REACTION BETWEEN NICKEL AND ZINC

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The main defect of the teaching of Tamman, Hedvall and Jander [1-4] on solid-phase reactions is the underevaluation of the role of the liquid and vapor phases. Soviet scientists [5-9] have exposed the scientific and methodological untenability of the so-called "classical" doctrine of solid-phase reactions and in their publications they have constantly emphasized the particularly important role of gases and liquids in the mechanism of reactions between solid substances. Actually, many reactions in solid phases only start to take place in practice when liquid or gaseous substances are formed.

We have studied the chemical interaction in the solid-phase system of pulverized nickel and zinc, and have shown that the reaction between them proceeds only with fusion of the readily fusible component (zinc). On the other hand, as evident from the phase diagram of the system Ni–Zn [10], apart from the wide region of the α-solid solution of zinc in nickel, the formation has been noted of the compounds NiZn, $NiZn_3$, Ni_2Zn_{15} (Fig. 1). It is perfectly clear that in the case of heated powders we are concerned with a non-equilibrium system; that phase corresponding to the given composition in the equilibrium phase diagram need not necessarily be formed. Such diagrams are obtained as a rule by heating the starting mixture above its melting point and then cooling the melt in order to determine the equilibrium temperatures of the liquid - crystal transition. In this sense the phase diagrams are "top-to-bottom" diagrams. In our case we study the "bottom-to-top" diagram of solid-phase reactions, and we investigate the characteristics of the non-equilibrium system in dependence on the nature and composition of the starting solid substances. This technique has direct bearing on powder metallurgy. Metal ceramics was little concerned with the sintering of powders of various metals [11], and recently alloying elements have begun to be introduced into powder metallurgy. In this connection a great contribution to solution of the chemical problems of the sintering of metal powders of various types will be made by a knowledge of the general laws of chemical interaction in non-equilibrium physical chemical systems whose study is indissolubly linked with the investigation of solid-phase reactions.

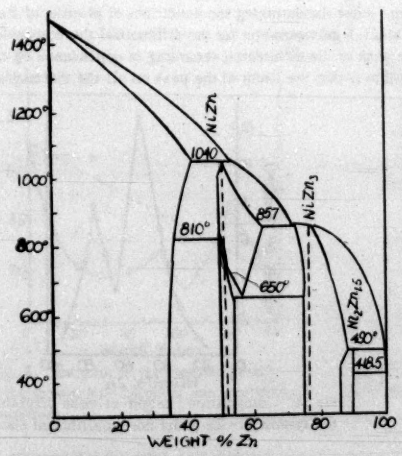

Fig. 1. Phase diagram of the system Ni–Zn

EXPERIMENTAL

As starting materials we used electrolytic nickel powder (99.8 % Ni) and ordinary zinc dust. The latter contained up to 2% zinc oxide and traces of iron (spectrally detected). The crystal structure of the powders was determined roentgenographically. Chemical interaction of the components is observed on heating mixtures of nickel and zinc powders and can be demonstrated in various ways.

Thermographic method. Thermograms were plotted with a Kurnakov pyrometer. Controlled thermoregulation was effected with the help of a thermocontrol complex and a thyratron relay assembled in a rotary-phase scheme [12]. The Pt–Pt, Rh combined thermocouple was calibrated by the potentiometric method [13]. Al_2O_3 or nickel powder was taken as the standard substance [14]. The reaction block was kept in a CO_2 atmosphere throughout the whole recording period. The thermographic data show that for all compositions starting approximately from 15 to 95% * Zn we have single-type heating curves. A typical thermogram for a mixture containing 30% zinc is plotted in Fig. 2. On the equilibrium phase diagram of the system Ni–Zn this composition corresponds to the region of the solid solution of zinc in nickel (Fig. 1).

* The percentages throughout are by weight, and the ZnO content of the powder was taken into account when comparing mixtures.

As the typical thermogram shows, the chemical interaction of nickel with zinc is accompanied by liberation of a large amount of heat. The diagram contains a small endothermic of melting of zinc and a large exothermic peak both on the simple and on the differential recording. In spite of the high resistances in the circuit of the combination thermocouple*, the deviation of the luminous traces in the direction of exothermicity is only registered at the start; therefore in Fig. 2 their imaginary trace on photographic paper is shown as a broken line. Only the return of the luminous traces at the termination of the reaction is clearly and sharply developed on the photographic paper. It should be added that the heating curve of zinc powder is characterized by one endothermic of its melting, while the thermogram of pure nickel has no thermal effects at all in the investigated temperature interval (up to 500-550°) (Fig. 3). Nor is any thermal effect detected on repeated recording of the heating curve of mixtures which registered an endothermic and a characteristic exothermic peak on the primary thermogram. We do not reproduce the second thermogram, for example, for a mixture containing 52.7% Zn, for it resembles the heating curve of nickel powder (Fig. 3). Consequently zinc reacts as a whole with nickel when heated; the system becomes essentially single-phase, so that the second thermogram contains neither an exothermic nor an endothermic.

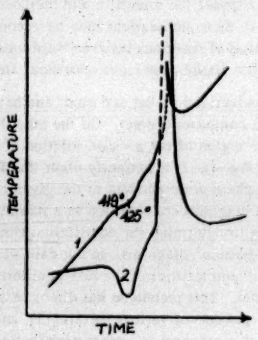

Fig. 2. Heating curve of a mixture of 70% Ni and 30% Zn.
1 - simple recording; 2 - differential recording.

As indicated above, Fig. 2 is a typical thermogram (approximately 15 to 95% Zn), while on the heating curves of other compositions (approximating to the pure components) the exothermicity is very weakly manifested even on the differential recording ($R_{differ.}$ = 55,000 Ω). Of course thermograms with clearly marked thermal effects are obtained also for these compositions when the sensitivity of the thermocouple differential is increased (reduced resistance).

Consequently, judging by the thermograms, it can be assumed that the interaction of nickel with zinc bears an explosive autocatalytic character from the instant of appearance of fused zinc in the mixture. The thermographic treatment of such autocatalytic reactions has been considered in detail elsewhere [15,16]. There is no doubt that nickel practically reacts with zinc only on fusion of the latter, i.e., the reaction proceeds with very close participtation of the liquid phase. The explosive character of the reaction itself is explained by the transition of zinc into the fused state. In order to establish whether the formation of any phases in the system Ni—Zn is accompanied by an explosive reaction with a sharp exothermic peak, we plotted a composition / height-of-peak diagram. After standardizing the conditions of plotting of the heating curves (total mass of mixtures 4 g, resistance to the M-21-1 galvanometer for the differential thermocouple 145,000 Ω, Ni standard, etc.), we measured the height of the peak of the differential recording in dependence on composition (Fig. 4). Another circumstance which made this possible is that the width of the peak on all the thermograms

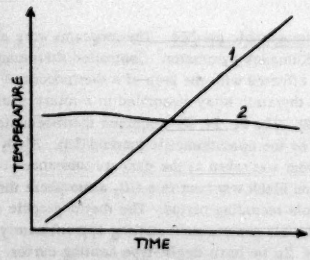

Fig. 3. Heating curve of nickel powder.
1 - simple recording; 2 - differential recording.

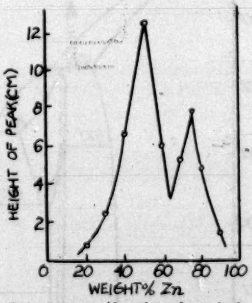

Fig. 4. Composition / height-of-peak diagram of the system Ni—Zn under non-equilibrium conditions.

* R_{simple} = 5,500 Ω ; $R_{differ.}$ = 55,000 Ω .

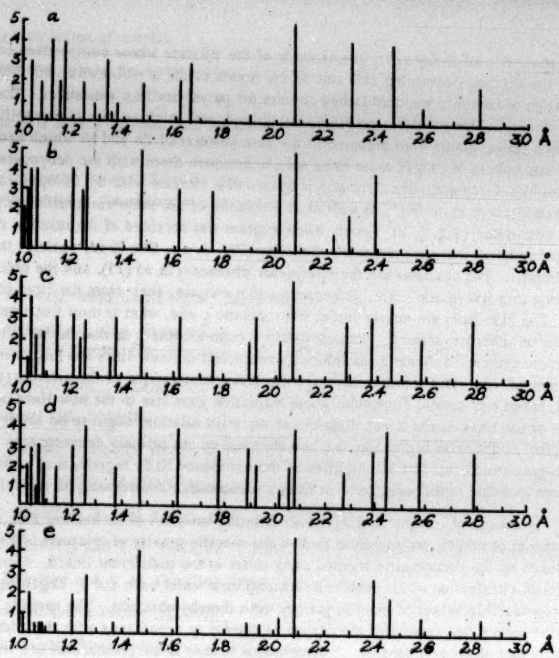

Fig. 5. Schemes of X-ray diagrams. Explanation in text.

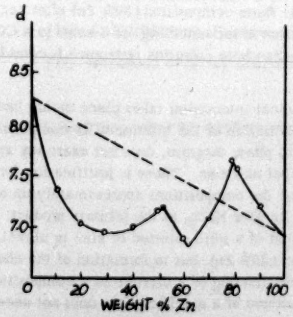

Fig. 6. Isotherm of the specific gravity of the system Ni–Zn under non-equilibrium conditions.

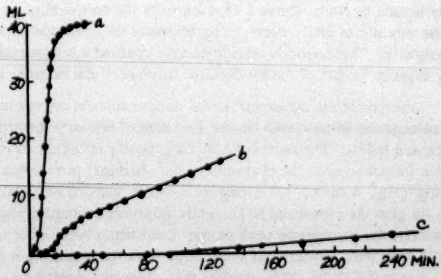

Fig. 7. Corrosion curves of mixture of the composition 70% Ni and 30% Zn.
Explanation in text.

in substantially the same at a standard rate of rotation of the pyrometer drum. As we see from Fig.4, the composition/height-of-peak plot has two sharp maxima which exactly coincide with the ordinates of the compounds NiZn and $NiZn_3$ in the phase diagram (Fig. 1).

X-ray structural analysis. An X-ray analysis was made of the mixture whose composition corresponded to the compound NiZn and of the mixture containing 30% zinc in the region of the α -solid solution. The debyeograms were plotted with $K_{\alpha\beta}$ radiation of iron in a standard Debye camera for polycrystalline substances. The samples were prepared in the following manner. The powder, very finely pulverized, was stuck on to a glass capillary with a diameter of 0.3 - 0.5 mm. At first debyeograms were prepared of the pure powders of Zn and Ni which had been heated beforehand to 500° in an atmosphere of CO_2 in order to be able to compare them with the debyeograms of the mixtures after sintering (Fig. 5, a, b). X-ray diagrams were also prepared of a mixture with the composition NiZn (Fig. 5, c) after plotting of the heating curve up to 500°, as well as of a mixture of the same composition after annealing for 6 hours at 500° in a CO_2 atmosphere (Fig. 5, d). Finally, a debyeogram was obtained of the mixture containing 30% Zn after plotting of the heating curve without subsequent annealing (Fig. 5, e). The X-ray patterns in Fig. 5 are in the above order (top to bottom). The abscissas are the interplanar distances (in A) [17], and the ordinates are the intensities classified according to a five-grade scale. Schemes a and b contain, apart from the lines of the pure metals, lines of ZnO and NiO. The zinc lines are nearly absent from scheme c and, what is most important, new lines are present which do not appear on schemes a and b. Scheme d differs from scheme c in that the new lines already observed on scheme c are now more intense. Scheme e resembles c except that the new lines are less intense. This is direct evidence of the formation not of a solid solution, although the taken composition of the mixture (30% Zn) falls in the region of its formation, but of a chemical compound whose formation gave rise to the new lines in schemes c and d. Moreover, the intensity of the lines on the X-ray diagrams of the solid solutions ought to be lower and the intensity of the dense background (fog) ought to be higher than we had observed on our primary debyeograms. In other words the character of the debyeograms indicates initial formation of the compound NiZn regardless of whether we start from a composition exactly corresponding to this compound or from a composition considerably to the left of it (30% Zn).

Specific gravity. A change of volume is observed on sintering mixtures of nickel and zinc, especially for compositions with a high content of nickel; we therefore studied the specific gravity of mixtures of various compositions. Determinations were made by the pycnometric method using water as the indifferent liquid. Special attention was given to the most thorough elimination of air bubbles by heating on a water bath and by degassing in a vacuum desiccator; satisfactorily reproducible values of specific gravity were thereby obtained. The specific gravity curve is plotted in Fig. 6 in which the broken line represents the change of density in accordance with the additivity rule in the absence of chemical interaction of the components. A conspicuous feature is the presence of two maxima on the specific gravity isotherm (25°) whose composition again corresponds to the ordinates of the chemical compounds NiZn and $NiZn_3$.

Corrosion. We studied the corrosion of some compositions in 1 N HCl solution by the method of displacement of hydrogen from the acid. As an example, we show in Fig. 7 the results of corrosion tests on a composition with 30% Zn. Curve a shows the solution of the mechanical mixture (without sintering); each component had previously been separately heated to 500°. Curve b characterizes the corrosion of a mixture of the same composition (30% Zn) after heating of the mixture to 500°; curve b characterizes the corrosion of the same mixture after annealing for 6 hours in a CO_2 atmosphere. The corrosion tests indirectly confirm the formation of new phases whose corrosion resistance is considerably superior to that of the mechanical mixture of the original substances.

Analysis of all the experimental data enables us to conclude that chemical interaction takes place during heating of mixtures of powdered Ni and Zn; here, of primary importance is the formation of the intermetallic compounds NiZn and $NiZn_3$. The compound Ni_2Zn_{15}, poorly reflected on the equilibrium phase diagram, does not exert any appreciable influence upon the character of the chemical interaction between nickel and zinc. There is justification for proposing (Figs. 4 and 6) that during solid-phase reaction of nickel with zinc all the compositions approximately up to 63% Zn give the compound NiZn, while mixtures containing more than 63% Zn give $NiZn_3$ as the primary product. Consequently, the exothermic peak on Fig. 2 evidently relates not to the formation of a solid solution of zinc in nickel, as should have been expected in accordance with the equilibrium phase diagram (30% Zn), but to formation of the chemical compound NiZn. This signifies that under non-equilibrium conditions the heating of a mixture of a composition belonging, according to the equilibrium diagram, in the region of stable existence of a specific phase does not necessarily lead to this phase.

Hence the equilibrium phase diagram (top-to-bottom diagram) evidently cannot serve for evaluation of the chemical interaction of components under non-equilibrium conditions (bottom-to-top diagram).

SUMMARY

1. The solid-phase interaction of nickel with zinc was studied by physical chemical methods.

2. The significance of the liquid phase in the mechanism of solid-phase reactions was illustrated by the example

of the chemical interaction of metals.

3. The decisive role of the compounds NiZn and $NiZn_3$ during chemical interaction of nickel and zinc was noted.

4. For the first time a composition/height-of-peak-of-the-differential-recording diagram was plotted and interpreted.

5. It was suggested that equilibrium phase diagrams (top-to-bottom) cannot serve as a basis for precise evaluation of the character of the chemical interaction of components under non-equilibrium conditions (bottom-to-top diagram).

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* Consultants Bureau Translation, p. 45, p. 523.
** Consultants Bureau Translation, p. 629, p. 303, p. 559.
*** Consultants Bureau Translation, p. 1199, p. 1325,
**** Consultants Bureau Translation, p. 743.

COMPLEX FORMATION AND DOUBLE DECOMPOSITION IN THE RECIPROCAL SYSTEM OF THE FLUORIDES AND SULFATES OF LEAD AND SODIUM

V. A. Gladushchenko and A. G. Bergman

The study of the system Na, Pb‖F, SO_4 is part of a systematic investigation of fluoride-sulfate reciprocal systems with participation of salts of lead and alkali metals.

Examination of the chloride-sulfate reciprocal system Na, Pb‖Cl, SO_4 revealed the presence inside the square of an extensive field corresponding to the binary compound $Na_2SO_4 \cdot 2PbSO_4$ [1].

The objective of the present investigation was to clarify the character of the behavior of the compound $Na_2SO_4 \cdot 2PbSO_4$ in the fluoride-sulfate reciprocal system, and to elucidate the type of this system. The thermal effect of the double decomposition reaction was 0.615 kcal/equiv. in the direction of the components Na_2SO_4, PbF_2. On one side of the square there is a compound $Na_2F_2 \cdot Na_2SO_4$ melting without decomposition at 782°. The remaining three sides of the square constitute simple eutectic systems.

EXPERIMENTAL

The investigation was carried out by the visual-polythermic melting method, using a platinum crucible and platinum stirrer, Au, Pt, Pd/Pt, Rh thermocouple, and a 40 mV millivoltmeter.

All calculations are reported in equimolar percentages. Sodium and lead fluorides were prepared by interaction of twice-distilled hydrofluoric acid with chemically pure sodium carbonate and lead carbonate. The sodium sulfate was twice recrystallized. Lead sulfate was prepared by precipitation of lead nitrate with sulfuric acid.

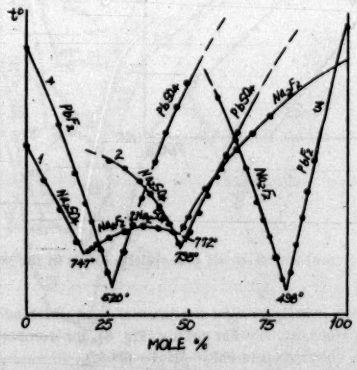

Fig. 1. Melting point diagrams of the binary systems. 1 - Na_2F_2–Na_2SO_4, 2 - Na_2SO_4–$PbSO_4$, 3 - Na_2F_2–PbF_2, 4 - PbF_2–$PbSO_4$.

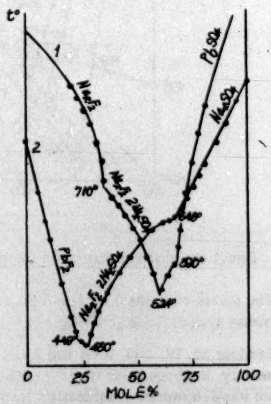

Fig. 2. Diagonal sections of the system. 1 - diagonal of Na_2F_2–$PbSO_4$, 2 - diagonal of PbF_2–Na_2SO_4.

Melting points of the salts: NaF 990°, PbF_2 860°, Na_2SO_4 884°, $PbSO_4$ 1100°.

Binary systems. 1) Na_2F_2–Na_2SO_4. This has been previously investigated [2,3]. Our data (Fig. 1, 1) confirmed the existence of the binary compound $Na_2F_2 \cdot 2Na_2SO_4$ melting without decomposition at 784° and 33.5% Na_2F_2.

2) Na_2SO_4 - $PbSO_4$ (Fig. 1, 2). Previously studied [4, 3]; repeated by us. The system has a eutectic point at 735° and 47.0% $PbSO_4$. 3) Na_2F_2 – PbF_2 (Fig. 1, 3). Previously studied [5] and repeated by us. Eutectic point at 498° and 19% Na_2F_2. 4) PbF_2–$PbSO_4$ (Fig. 1, 4). Studied by us. System with a eutectic point at 520° and 26.5% $PbSO_4$.

Diagonal sections. 1) Na_2F_2–$PbSO_4$ (Table 1, Fig. 2, 1). 2) PbF_2–Na_2SO_4 (Table 1, Fig. 2, 2).

The ternary reciprocal system. The crystallization surface was determined by a study of 18 internal sections (Fig. 3). In Tables 3 and 4 are set forth the data for the most important sections. The projection of the spatial diagram of the reciprocal system (Na, Pb‖F, SO_4) on to the square of composition indicates the formation of 7 fields of crystallization (Fig. 6).

The compound $Na_2F_2 \cdot 2Na_2SO_4$, melting without decomposition, is located in the interior of the square and occupies 22.1% of its area. Under the influence of salt solvents this compound is transformed inside the square into one melting with decomposition.

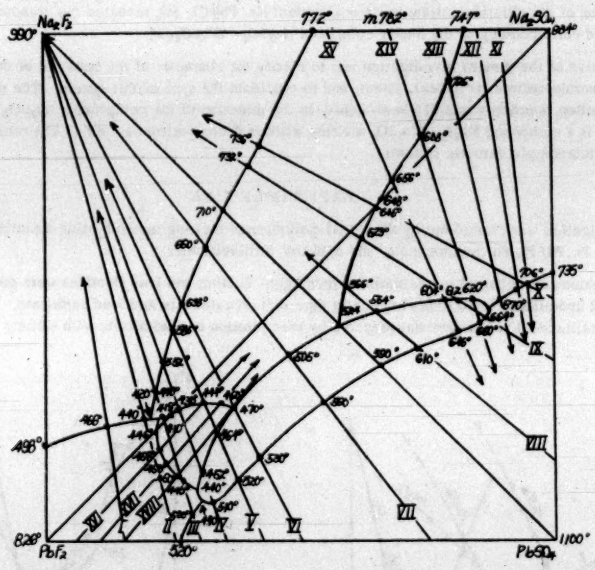

Fig. 3. Directions of the investigated internal sections.

The square contains the field of $Na_2SO_4 \cdot 2PbSO_4$ (6.4% of area) which, in all probability, exists in the solidus of the binary system Na_2SO_4–$PbSO_4$.

Sections III, IV, XVI, XVII and XVIII (Figs. 4 and 5) helped to bring to light one internal field which belongs to the ternary, heterogeneous system (1.4% of area). Its pole is arbitrarily fixed at point x (Fig. 6), the composition of which was determined graphically. Its conventional formula corresponds to $PbF_2 \cdot 3NaF \cdot 2PbSO_4$.

The reciprocal system Na, Pb‖F, SO_4 has a complex form of triangulation due to the existence of three fields. As we see from Fig. 6, the square of composition is split up by secants, starting from the poles of the above-mentioned compounds, into 6 phase triangles. To each triangle corresponds one invariant ternary eutectic or transition point; their melting points and compositions are detailed in Table 2.

The experimental data for the composition and melting points of these points were checked and corrected on the bases of the projection of the lines of common crystallization on to the side of PbF_2–$PbSO_4$ (Fig. 7).

TABLE 1

Diagonal sections

$Na_2F_2 - PbSO_4$				$PbF_2 - Na_2SO_4$			
% $PbSO_4$	t	% $PbSO_4$	t	% Na_2SO_4	t	% Na_2SO_4	t
23	872°	53	595°	7	670°	35	530°
26	850	56	565	10	618	40	556
29	826	57	549	13	560	45	580
32	795	59	535	16	515	50	608
34	750	62	560	18	486	55	627
35	724	65	580	20	460	60	640
36	706	68	640	22	443	62	643
38	698	71	700	24	437	65	647
41	684	74	757	26	455	68	662
44	666	77	806	28	472	71	680
47	643	80	856	30	490	74	700
50	624			33	511	77	720

Points of intersection:

710°, 35% $PbSO_4$;
524°, 58% $PbSO_4$;
590°, 67% $PbSO_4$;

Points of intersection:

446°, 21% Na_2SO_4;
430°, 25% Na_2SO_4;
648°, 66% Na_2SO_4.

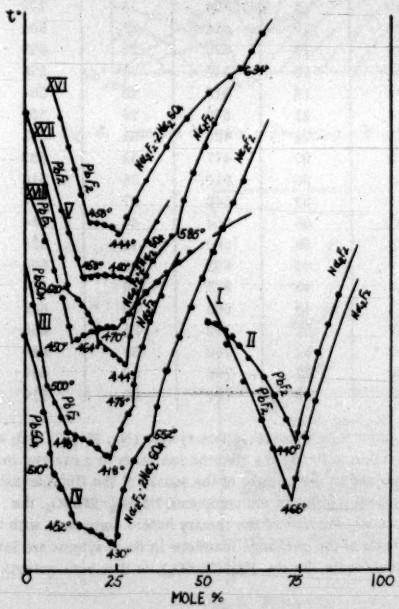

Fig. 4. Internal sections of the system from I to V and from XVI to XVIII.

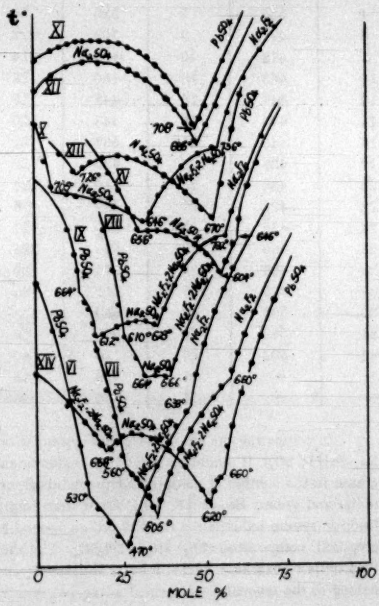

Fig. 5. Internal sections of the system from VI to XV.

TABLE 2

Point	Melting point	Name of point	Composition (in %)				Equilibrium phases
			$PbSO_4$	Na_2F_2	PbF_2	Na_2SO_4	
P_I	524°	Transition	16.0	–	41.5	42.5	Na_2SO_4 + A + B*
P_{II}	420	Transition	20.0	24.0	56.0	–	Na_2F_2 + A + PbF_2
E_{III}	410	Eutectic	21.5	24.5	54.0	–	A + X + PbF_2
E_{IV}	440	Eutectic	28.5	10.5	61.0	–	X + B + PbF_2
Q	470	Transition	37.0	26.0	37.0	–	A + B + X
E_V	490	Eutectic	32.5	5.5	62.0	–	B + $PbSO_4$ + PbF_2

TABLE 3

Internal sections of the reciprocal system Na, Pb || F, SO_4

Section III		Section IV		Section V		Section VI		Section VII	
30% $PbSO_4$ 70% PbF_2 } Na_2F_2		35% $PbSO_4$ 65% PbF_2 } Na_2F_2		42% $PbSO_4$ 58% PbF_2 } Na_2F_2		50% $PbSO_4$ 50% PbF_2 } Na_2F_2		75% $PbSO_4$ 25% PbF_2 } Na_2F_2	
% Na_2F_2	t	% Na_2F_2	t	% Na_2F_2	t	% Na_2F_2	t	% Na_2F_2	t
2	580°	5	570°	5	640°	0	780°	15	740°
4	535	7	525	10	560	5	724	18	700
6	497	8	503	12	530	10	624	21	654
8	478	10	490	14	515	13	590	23	623
10	463	13	460	16	506	15	546	25	578
12	447	15	448	18	494	18	516	28	554
14	444	18	443	20	476	21	500	29	550
16	440	21	437	21	468	24	484	31	543
18	436	23	432	22	462	27	477	33	532
20	430	25	440	24	456	30	510	35	518
22	422	27	487	26	450	33	540	37	523
24	430	30	520	27	447	36	564	40	554
26	450	33	540	28	476	39	590	43	580
28	468	36	574	30	510	42	608	46	603
30	498	39	611	33	540	45	625	49	620
32	536	42	648	35	554	48	668	52	636
34	562	45	680	38	572	51	702	55	650
42	592	48	710	40	582	54	740	58	660
–	–	51	738	43	620	57	766	60	680
–	–	54	764	46	648	60	790	63	710

In comparing the chloride-sulfate system with the corresponding fluoride-sulfate system (Na, Pb || Cl, SO_4 and Na, Pb || F, SO_4), it should be noted that replacement of the chlorine ion by the fluorine ion leads to a marked increase in the number of complex compounds both on the sides and in the interior of the square of the fluoride-sulfate reciprocal system Na, Pb || F, SO_4. Apart from formation for both systems of the compound $Na_2SO_4 \cdot 2PbSO_4$, the fluoride system exhibits the field of the compound $Na_2F_2 \cdot 2Na_2SO_4$ and that of the ternary hetero compound with the proposed composition $PbF_2 \cdot 3NaF \cdot 2PbSO_4$. The thermal effects of the exchange reactions in these sytems are less than unity (0.615 kcal/equiv. for Na, Pb || F, SO_4 and 0.88 kcal/equiv. for Na, Pb || Cl, SO_4), so that both systems belong to the reversible-reciprocal adiagonal type.

* A – $Na_2F_2 \cdot 2Na_2SO_4$, B – $Na_2SO_4 \cdot 2PbSO_4$, X – $PbF_2 \cdot 3NaF \cdot 2PbSO_4$.

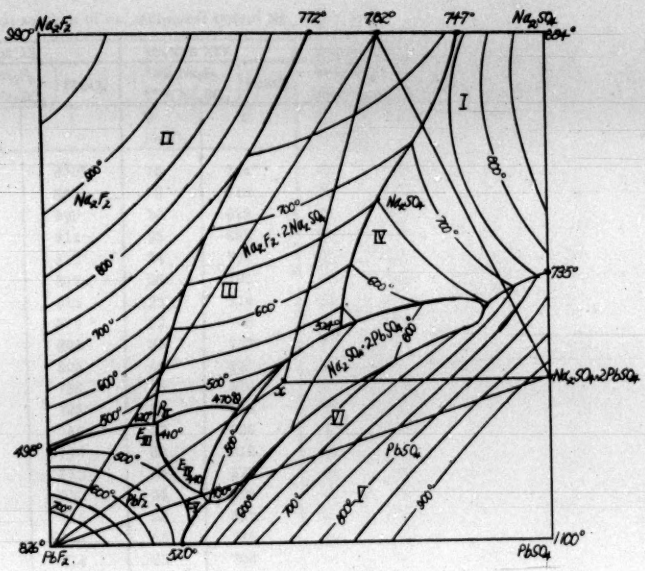

Fig. 6. Liquidus diagram of the reciprocal system Na, Pb||F, SO_4.

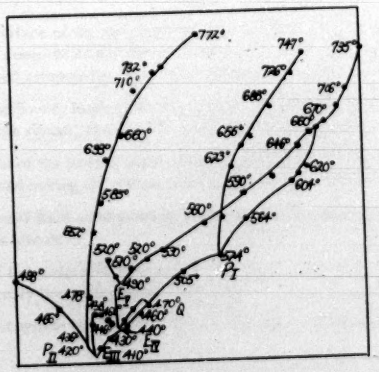

Fig. 7. Projection of lines of common crystallization on to the $PbF_2 - PbSO_4$ side.

TABLE 4

Internal sections of the reciprocal system Na, Pb || F, SO_4

Section XI		Section XIV		Section XV		Section XVI		Section XVIII	
10% Na_2F_2 90% Na_2SO_4 } $PbSO_4$		33% Na_2F_2 67% Na_2SO_4 } $PbSO_4$		45% Na_2F_2 55% Na_2SO_4 } $PbSO_4$		5% $PbSO_4$ 95% PbF_2 } Na_2SO_4		15% $PbSO_4$ 85% PbF_2 } Na_2SO_4	
% $PbSO_4$	t	% $PbSO_4$	t	% $PbSO_4$	t	% Na_2SO_4	t	% Na_2SO_4	t
6	800°	15	724°	20	727°	10	572°	5	564°
8	806	18	710	23	707	12	542	8	532
10	809	20	698	26	686	14	518	10	503
13	811	22	692	29	660	16	490	12	473
15	812	24	702	32	658	18	460	14	458
18	812	26	707	35	658	20	460	16	464
20	812	29	710	38	658	22	460	18	468
23	810	32	708	41	652	24	458	20	470
26	808	35	703	44	648	26	448	22	472
29	805	40	691	47	638	28	466	24	472
33	798	45	670	50	628	30	484	26	478
35	793	50	643	52	618	33	408	28	487
38	783	52	630	54	606	39	542	30	498
41	770	53	612	56	618	45	574	33	509
44	752	55	622	58	638	51	600	36	520
47	733	56	628	60	638	57	622	39	531
49	715	58	692	63	708	60	630	42	540
51	718	60	716	66	736	63	648	45	553
53	774	63	755	—	—	66	668	—	—
56	765	71	790	—	—	70	696	—	—
59	788	74	822	—	—	—	—	—	—

SUMMARY

1. The liquidus surface of the reciprocal system Na, Pb || F, SO_4 consists of seven fields of crystallization, four of which belong to components and three to compounds: $Na_2F_2 \cdot 2Na_2SO_4$, $Na_2SO_4 \cdot 2PbSO_4$ and a ternary hetero compound of the proposed composition $PbF_2 \cdot 3NaF \cdot 2PbSO_4$.

2. The binary compound, $Na_2F_2 \cdot 2Na_2SO_4$, occupying a considerable part of the surface of the square, is perfectly stable inside the system, and its phase enters into the composition of the ternary eutectic point E_{III} 410°.

3. The boundaries of the internal field corresponding to the compound formed in the solidus of the binary system Na_2SO_4—$PbSO_4$ and having the composition $Na_2SO_4 \cdot 2PbSO_4$ were detected and defined.

4. A second internal field corresponding to the ternary hetero compound with the probable composition $PbF_2 \cdot 3NaF \cdot 2PbSO_4$ was revealed.

5. The square of the reciprocal system is split up by triangulating secants into six phase triangles to each of which corresponds a ternary invariant point: P_I 524°, P_{II} 420°, E_{III} 410°, E_{IV} 440°, E_V 490° and Q 470°.

6. The reciprocal system Na, Pb || F, SO_4 is an example of an adiagonal system with an internal field.

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TABLE 4

Internal relations of the [illegible] section [illegible]

| Section XI | | |

RECIPROCAL SOLUBILITY OF SALTS IN THE SYSTEM OF THE CHLORIDES AND NITRATES OF BARIUM AND CALCIUM FROM TEMPERATURES OF COMPLETE SOLIDIFICATION TO +60°

L. N. Uspenskaya, N. P. Glushkova and A. G. Bergman

The system $Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot} \| Cl^{\cdot}$, $NO_3^{\cdot}-H_2O$ as a whole has not previously been investigated. The melting method has been applied only to individual portions of this system as component elements of other systems [1,2]. Results from solubility determinations of a limited and inadequate character also appear in the handbook literature [3,4].

Great practical interest is attached to a solution of the problem of the change of direction of double decomposition in solutions and melts with change of temperature. From this aspect our communication on the reciprocal system $Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot} \| Cl^{\cdot}$, NO_3-H_2O in the temperature range from complete freezing to +60° has supplemented the data of an investigation of the solubility of the same reciprocal system at 80, 100 and 120°, previously undertaken by us [8].

EXPERIMENTAL

Investigation of the system from complete solidification to +60° was carried out by the visual-polythermal method in the usual apparatus with tube, thermometer and stirrer. The low temperatures were reached with the help of solid carbon dioxide.

Thermometer readings were taken on the appearance of the first crystals and disappearance of the last crystals.

The following systems were studied: 1) $BaCl_2-Ba(NO_3)_2-H_2O$; 2) $CaCl_2-Ba(NO_3)_2-H_2O$ (diagonal section); 3) $BaCl_2-Ca(NO_3)_2-H_2O$ (diagonal section).

1. System $BaCl_2-Ba(NO_3)_2-H_2O$. The solubility of the salts of this sytem has been partly studied at +20 and 30° [5]. Data for the solubility of the systems $BaCl_2-H_2O$ and $Ba(NO_3)_2-H_2O$ have been reported [4,6,7]. We repeated measurements on both systems. Results of study of the ternary system between the temperatures of complete solidification and 120° are detailed in Tables 1-3 and plotted in Figs. 1 and 2. The solubility curves of the 20, 40 and 60° isotherms correspond to the dihydrate of barium chloride; the solubility curve of the 80° isotherm corresponds to barium chloride monohydrate; the solubility curves of the 100 and 120° isotherms correspond to anhydrous barium chloride.

In Fig. 1 we have traced out hypothetically the fields of the dihydrate and monohydrate of barium chloride on the basis of data in [6] and of the projection of the polytherm of the system $BaCl_2-Ba(NO_3)_2-H_2O$ onto the side of $BaCl_2-H_2O$.

2. System $CaCl_2-Ba(NO_3)_2-H_2O$ (diagonal section). Many authors have studied the system $CaCl_2-H_2O$ [3,7]; we have studied it up to 29% $CaCl_2$ (−49.8°).

Results of our study of the whole of the ternary system from the temperature of complete solidification up to +60°, set forth in Tables 4 to 6 and plotted in Figs. 3 and 4, have supplemented our data previously obtained at 80, 100 and 120° [8].

On inspecting the tables and solubility isotherms of the system $CaCl_2-Ba(NO_3)_2-H_2O$ we observe a sharp drop in solubility of barium nitrate in presence of calcium chloride, which may be due to the high degree of hydration of calcium chloride.

The solubility isotherms consist of two branches – of barium nitrate and barium chloride. The eutonic point and crystallization curve of calcium chloride could not be experimentally determined, since at 20, 40 and 60° both are very close to the $CaCl_2-H_2O$ ordinate.

The system is an unstable, diagonal, reciprocal system of $Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot} \| Cl^{\cdot}$, $NO_3^{\cdot}-H_2O$. The arrangement of the isotherms indicates that the field of barium chloride is rather slanting.

At the $CaCl_2$ corner in Fig. 4, the isotherms are closely crowded towards the ordinate. The triple eutonic contains approximately 99.8 mole % $CaCl_2$, 0.20 mole % $Ba(NO_3)_2$ and 1200 moles water per 100 moles of total anhydrous salts.

TABLE 1

Solubility of salts in the system $BaCl_2-Ba(NO_3)_2-H_2O$ (in weight %)

Systems investigated	20° isotherm				40° isotherm				60° isotherm			
	content of salts and water			bottom phases	content of salts and water			bottom phases	content of salts and water			bottom phases
	$BaCl_2$	$Ba(NO_3)_2$	H_2O		$BaCl_2$	$Ba(NO_3)_2$	H_2O		$BaCl_2$	$Ba(NO_3)_2$	H_2O	
$Ba(NO_3)_2-H_2O$	–	8.50	91.50	$Ba(NO_3)_2$	–	12.50	87.50	$Ba(NO_3)_2$	–	16.17	83.22	$Ba(NO_3)_2$
$BaCl_2-Ba(NO_3)_2-H_2O$	4.64	7.50	87.86		4.47	10.70	84.83		4.30	14.00	81.70	
	9.33	6.70	83.97		9.01	9.70	81.29		8.75	12.50	78.76	
	14.03	6.50	79.47		13.65	9.00	77.35		13.25	11.70	75.05	
	18.76	6.20	75.04		18.28	8.60	73.12		17.80	11.00	71.20	
	20.64	6.20	73.16		21.20	8.20	70.60		20.63	10.30	69.07	
	21.55	6.30	72.15		21.14	8.10	70.76		22.65	10.20	67.15	
	24.60	6.08	69.46	$BaCl_2 \cdot 2H_2O + Ba(NO_3)_2$	22.95	8.20	68.85		28.20	7.18	65.72	$BaCl_2 \cdot 2H_2O$
	26.40	2.20	71.40	$BaCl_2 \cdot 2H_2O$	26.00	7.40	66.60	$BaCl_2 \cdot 2H_2O + Ba(NO_3)_2$	29.12	5.67	65.21	
	27.00	1.09	71.91		26.50	5.88	67.62	$BaCl_2 \cdot 2H_2O$				
$BaCl_2-H_2O$	27.50	–	72.50		30.50	–	69.50		33.50	–	66.50	

TABLE 2

Solubility of salts in the system $BaCl_2-Ba(NO_3)_2-H_2O$ (in mole %)

Salt systems investigated	20° isotherm				40° isotherm				60° isotherm			
	content of salts		moles water per 100 moles anhydrous salts	bottom phases	contents of salts		moles water per 100 moles anhydrous salts	bottom phases	contents of salt		moles water per 100 moles anhydrous salts	bottom phases
	$BaCl_2$	$Ba(NO_3)_2$			$BaCl_2$	$Ba(NO_3)_2$			$BaCl_2$	$Ba(NO_3)_2$		
$Ba(NO_3)_2-H_2O$	–	100	15630.70	$Ba(NO_3)_2$	–	100	10145.00	$Ba(NO_3)_2$	–	100	7260.50	$Ba(NO_3)_2$
$BaCl_2-Ba(NO_3)_2-H_2O$	43.62	56.38	9579.30		34.34	65.66	7536.10		27.82	72.18	6104.00	
	63.64	36.36	6619.30		53.86	46.14	5606.00		46.77	53.23	4859.00	
	72.99	27.01	4775.40		65.56	34.44	4289.10		58.72	41.28	3839.00	
	79.15	20.85	3667.50		72.70	27.30	3358.00		67.02	32.98	3095.00	
	80.63	19.32	3304.10		76.40	23.60	2939.00		69.95	30.05	2863.00	
	81.90	18.10	3136.50		76.58	23.42	2960.00		71.53	28.47	2765.50	
	83.60	16.40	2724.30	$BaCl_2 \cdot 2H_2O + Ba(NO_3)_2$	77.81	22.19	2695.00		73.63	26.37	2520.00	
	94.03	5.97	2394.80		81.60	18.40	2411.00	$BaCl_2 \cdot 2H_2O + Ba(NO_3)_2$	83.43	16.57	2163.90	$BaCl_2 \cdot 2H_2O$
	96.89	3.11	2970.80	$BaCl_2 \cdot 2H_2O$	84.97	15.03	2490.40		86.56	13.44	2240.90	
$BaCl_2-H_2O$	100	–	3056.10		100	–	2631.00	$BaCl_2 \cdot 2H_2O$	100	–	2292.30	

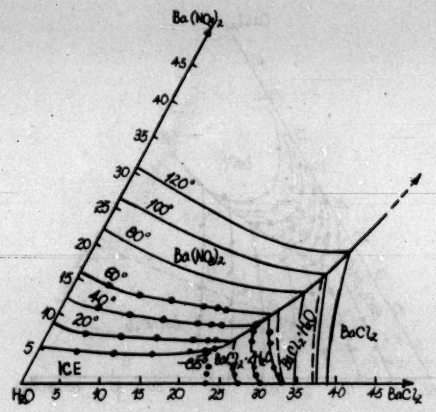

Fig. 1. Reciprocal solubility of salts (in weight-%) in the system $BaCl_2-Ba(NO_3)_2-H_2O$.

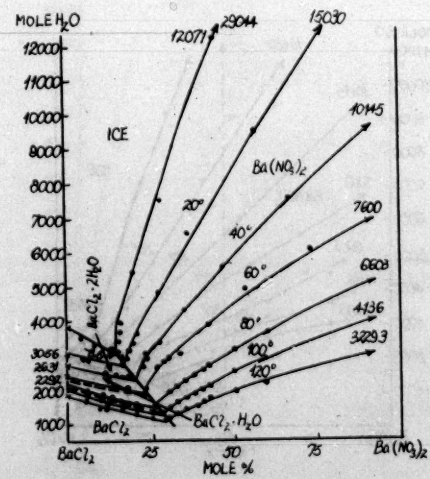

Fig. 2. Reciprocal solubility of salts (in mole-%) in the system $BaCl_2-Ba(NO_3)_2-H_2O$.

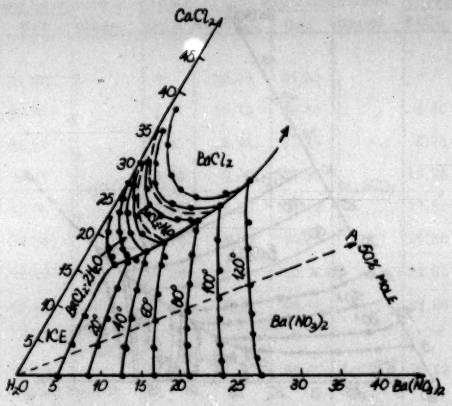

Fig. 3. Reciprocal solubility of salts (in weight-%) in the system $CaCl_2-Ba(NO_3)_2-H_2O$.
A) "Conversion line".

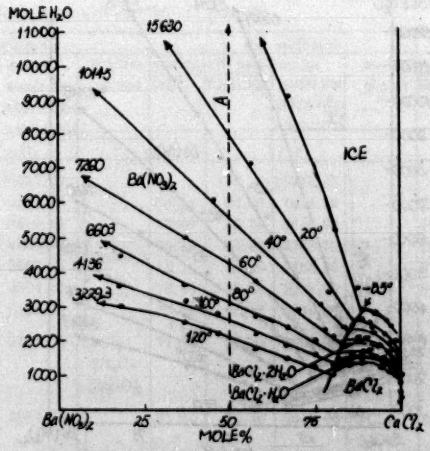

Fig. 4. Reciprocal solubility (in mole-%) of salts in the system $CaCl_2-Ba(NO_3)_2-H_2O$.
A) "conversion line".

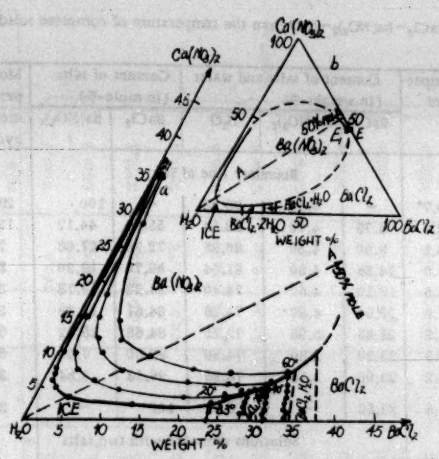

Fig. 5. a) Reciprocal salt solutions (in weight %) of the system $BaCl_2-Ca(NO_3)_2-H_2O$ at 20, 40 and 60°; b) Scheme of the complete polytherm system $BaCl_2-Ca(NO_3)_2-H_2O$ A) "line conversion".

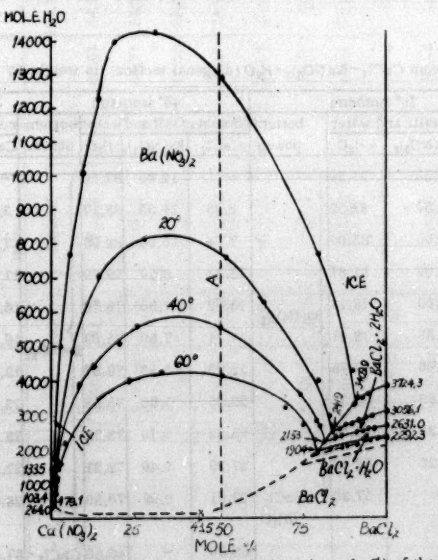

Fig. 6. Reciprocal salt solution (in mole %) of the system $BaCl_2-Ca(NO_3)_2-H_2O$.
A) "line conversion".

TABLE 3

Polytherms of the system $BaCl_2-Ba(NO_3)_2-H_2O$ from the temperature of complete solidification to + 60° (Figs. 1 and 2)

Salt systems investigated		Temperature	Content of salts and water (in weight-%)			Content of salts (in mole-%)		Moles water per 100 moles anhydrous salts	Bottom phases
			$BaCl_2$	$Ba(NO_3)_2$	H_2O	$BaCl_2$	$Ba(NO_3)_2$		
			Boundary line of ice						
$Ba(NO_3)_2-H_2O$		−0.7°	−	4.75	95.25	−	100	29044.0	Ice + $Ba(NO_3)_2$
	$BaCl_2-Ba(NO_3)_2-H_2O$	−2.1	4.76	4.70	90.54	55.88	44.12	12071.0	
		−3.1	9.50	4.50	85.95	72.92	27.08	7595.8	
		−4.0	14.36	4.30	81.34	80.70	19.30	5278.4	
		−6.5	19.10	4.50	74.40	84.22	15.78	3890.0	
		−7.8	20.94	4.80	74.26	84.61	15.39	3546.5	
		−8.2	21.85	5.00	73.15	84.68	15.32	3274.2	
		−8.3	23.20	2.30	74.50	92.60	7.40	3437.0	
		−8.2	23.00	1.15	75.85	96.18	3.84	3660.7	
$BaCl_2-H_2O$		−7.6	23.50	−	76.50	100	−	3724.3	Ice + $BaCl_2 \cdot 2H_2O$
			Solutions saturated with two salts						
$BaCl_2-Ba(NO_3)_2-H_2O$		−8.5°	22.50	5.10	72.70	84.55	15.45	3197.3	Ice + $BaCl_2 \cdot 2H_2O$ + + $Ba(NO_3)_2$
		20	24.50	6.08	69.42	83.54	16.46	2808.9	$BaCl_2 \cdot 2H_2O$ + + $Ba(NO_3)_2$
		40	25.80	8.40	65.80	79.40	20.60	2338.0	
		60	26.70	10.00	63.70	77.03	22.97	2120.5	

TABLE 4

Solubility of salts in the system $CaCl_2-Ba(NO_3)_2-H_2O$ (diagonal section) (in weight %)

Salt system investigated		20° isotherm				40° isotherm				60° isotherm			
		content of salts and water			bottom phases	content of salt and water			bottom phases	content of salt and water			bottom phases
		$CaCl_2$	$Ba(NO_3)_2$	H_2O		$CaCl_2$	$Ba(NO_3)_2$	H_2O		$CaCl_2$	$Ba(NO_3)_2$	H_2O	
$Ba(NO_3)_2-H_2O$		−	8.50	91.50	$Ba(NO_3)_2$	−	12.50	87.50	$Ba(NO_3)_2$	−	16.68	83.32	$Ba(NO_3)_2$
	$CaCl_2-Ba(NO_3)_2-H_2O$	3.98	7.50	88.52		3.83	11.00	85.17		3.66	14.80	81.54	
		8.00	7.00	85.00		7.74	10.00	82.26		7.48	13.00	79.52	
		12.13	6.00	81.87		11.80	8.50	79.70		11.44	11.30	77.26	
		16.25	5.00	78.75		15.82	7.50	76.68		15.39	10.00	74.61	
		17.79	3.80	78.41		17.11	7.50	75.39		16.74	9.50	73.76	
		20.24	2.00	77.76		19.93	3.50	76.57		19.54	5.40	75.01	
		23.07	0.60	76.33		22.85	1.60	75.65		22.50	3.00	74.50	
		25.62	0.30	74.08		25.52	0.70	73.78		25.32	1.50	73.18	
		27.43	0.25	72.32		27.39	0.40	72.21		27.31	0.70	71.99	
$CaCl_2-H_2O$		42.70	−	57.30	$CaCl_2 \cdot 6H_2O$	29.61	0.09	70.30		28.93	0.25	70.82	
						53.50	−	46.50	$CaCl_2 \cdot 4H_2O$	57.80	−	42.20	$CaCl_2 \cdot 2H_2O$

TABLE 5

Solubility of salts in the system $CaCl_2-Ba(NO_3)_2-H_2O$ (diagonal section) (in mole %)

Salt system investigated	20° isotherm				40° isotherm				60° isotherm			
	Content of salts		moles water per 100 moles anhydrous salts	Bottom phases	Contents of salts		moles water per 100 moles anhydrous salts	Bottom phases	Contents of salts		moles water per 100 moles anhydrous salts	Bottom phases
	$CaCl_2$	$Ba(NO_3)_2$			$CaCl_2$	$Ba(NO_3)_2$			$CaCl_2$	$Ba(NO_3)_2$		
$Ba(NO_3)_2-H_2O$	–	100.0	15630.7	$Ba(NO_3)_2$	–	100.0	10145.0	$Ba(NO_3)_2$	–	100.0	9260.5	$Ba(NO_3)_2$
$CaCl_2-Ba(NO_3)_2-H_2O$	55.57	44.43	7611.9		45.03	54.97	6174.1		36.70	63.30	5048.9	
	72.40	27.60	4765.0		64.77	35.25	4313.3		57.50	42.58	3772.1	
	78.59	21.49	3364.0		77.50	23.50	3228.0		70.30	29.70	2921.9	
	88.45	11.55	2641.7		83.23	16.77	2488.3		78.21	21.79	2355.4	
	91.19	8.81	2491.8		84.40	15.60	2290.0		80.54	19.46	2194.0	
	96.00	4.00	2268.4		92.98	7.02	2201.9		89.48	10.52	2120.0	
	98.30	1.10	2018.3		97.30	2.70	1985.8		94.63	5.37	1932.1	
	99.48	0.52	1773.3		98.79	1.21	1762.7		97.56	2.44	1738.5	
	99.61	0.49	1620.0		99.39	0.61	1615.6		98.20	1.10	1608.0	
					99.87	0.13	1461.3		99.65	0.35	1493.8	
$CaCl_2-H_2O$	100	–	827.5	$CaCl_2 \cdot 6H_2O$	100.0	–	537.50	$CaCl_2 \cdot 4H_2O$	100.0	–	450.4	$CaCl_2 \cdot 2H_2O$

TABLE 6

Polytherms of the system $CaCl_2-Ba(NO_3)_2-H_2O$ from the temperature of complete solidification to +60° (Figs. 3 and 4)

Salt systems investigated		Temperature	Content of salts in water (in weight %)			Content of salts (in mole %)		Moles water per 100 moles anhydrous salts	Bottom phases
			$CaCl_2$	$Ba(NO_3)_2$	H_2O	$CaCl_2$	$Ba(NO_3)_2$		
					Boundary line of salt				
$Ba(NO_3)_2-H_2O$		−0.70°	–	4.75	95.25	–	100.0	29044.0	
	$CaCl_2-Ba(NO_3)_2-H_2O$	−2.5	4.09	4.74	91.17	66.90	33.10	9149.0	
		−5.70	8.22	4.40	86.38	81.45	18.55	5280.0	
		−8.2	12.40	3.80	83.80	88.00	12.00	3665.0	Ice + $Ba(NO_3)_2$
		−14.5	16.59	3.00	80.41	92.80	7.20	2810.3	
		−16.5	18.22	1.50	80.28	96.62	3.38	2627.6	
		−17.5	20.54	0.50	78.96	96.98	1.02	2346.4	
$CaCl_2-H_2O$		−49.8	30.22	–	69.78	100.0	–	1428.0	Ice + $CaCl_2 \cdot 4H_2O(\alpha)$
					Solutions saturated with two salts				
	$CaCl_2+Ba(NO_3)_2+H_2O$	−8.5°	15.50	4.30	81.20	89.43	10.57	2888.9	Ice + $CaCl_2 \cdot 6H_2O$ + $Ba(NO_3)_2$
		+20.0	16.10	5.10	78.80	88.10	11.90	2660.7	$CaCl_2 \cdot 6H_2O$ + $Ba(NO_3)_2$
		+40.0	17.11	7.50	75.39	84.33	15.67	2291.4	$CaCl_2 \cdot 4H_2O$ + $Ba(NO_3)_2$
		+60.0	18.50	8.70	72.80	83.34	16.66	2022.2	$CaCl_2 \cdot 2H_2O$ + $Ba(NO_3)_2$

TABLE 7

Solubility of salts in the system $BaCl_2-Ca(NO_3)_2-H_2O$ (diagonal section) (in weight %)

Salt systems investigated	20° isotherm				40° isotherm				60° isotherm			
	Contents of salts and water			Bottom phases	Contents of salts and water			Bottom phases	Contents of salts and water			Bottom phases
	$BaCl_2$	$Ca(NO_3)_2$	H_2O		$BaCl_2$	$Ca(NO_3)_2$	H_2O		$BaCl_2$	$Ca(NO_3)_2$	H_2O	
$BaCl_2-H_2O$	27.50	–	72.50	$BaCl_2 \cdot 2H_2O$	30.50	–	69.50	$BaCl_2 \cdot 2H_2O$	33.50	–	66.50	$BaCl_2 \cdot 2H_2O$
$BaCl_2-Ca(NO_3)_2-H_2O$	27.40	1.09	71.51		30.10	1.05	68.85		33.00	1.01	65.99	
	27.20	1.56	71.24		30.05	1.40	68.55		32.80	1.35	65.85	
	27.15	1.82	71.03		30.00	1.75	68.25		32.70	1.68	65.62	
	27.06	2.55	70.39		29.70	2.45	67.85		32.40	2.37	65.22	
	27.00	3.00	70.00		29.20	3.54	67.26		32.10	3.40	64.50	
	27.00	3.65	69.36		29.00	4.26	66.74		32.00	4.08	63.92	
	26.20	3.80	70.00	$Ba(NO_3)_2$	25.00	5.00	70.00	$Ba(NO_3)_2$	31.30	5.15	63.55	
	24.00	3.80	72.20		23.70	5.20	71.10		23.39	6.50	70.13	
	18.81	3.50	77.69		18.48	5.20	76.32		18.03	7.50	74.47	$Ba(NO_3)_2$
	10.00	4.50	85.50		9.00	6.80	84.20		11.50	8.85	79.65	
	6.50	5.60	87.90		5.70	9.43	84.87		7.00	11.62	82.38	
	3.50	7.24	89.26		4.40	11.95	83.65		5.50	14.17	80.33	
	2.26	9.50	88.24		2.80	14.58	82.62		1.80	28.00	70.20	
	2.26	9.60	88.14		2.05	18.00	79.95		0.99	34.67	64.38	
	1.20	14.82	83.98		0.56	34.80	64.64		–	77.50	22.50	$Ca(NO_3)_2$ [3]
	0.25	34.91	64.84		–	65.50	34.50					
$Ca(NO_3)_2-H_2O$	–	56.40	43.46	$Ca(NO_3)_2 \cdot 4H_2O$				$Ca(NO_3)_2 \cdot 4H_2O$				

TABLE 8

Solubility of salts in the system $BaCl_2-Ca(NO_3)_2-H_2O$ (diagonal section) (in mole %)

Salt systems investigated	20° isotherm				40° isotherm				60° isotherm			
	Content of salts		Moles water per 100 moles anhydrous salts	Bottom phases	Content of salts		Moles water per 100 moles anhydrous salts	Bottom phases	Content of salts		Moles water per 100 moles anhydrous salts	Bottom phases
	$BaCl_2$	$Ca(NO_3)_2$			$BaCl_2$	$Ca(NO_3)_2$			$BaCl_2$	$Ca(NO_3)_2$		
$BaCl_2-H_2O$	100	–	3056.1		100	–	2631.0		100	–	2292.3	
$BaCl_2-Ca(NO_3)_2-H_2O$	95.22	4.78	2869.7		95.75	4.25	2538.2		96.33	3.67	2223.6	
	93.22	6.79	2820.2		94.42	5.58	2486.6		95.05	4.95	2204.0	
	92.15	7.85	2790.6	$BaCl_2 \cdot 2H_2O$	93.08	6.92	2445.0	$BaCl_2 \cdot 2H_2O$	93.90	6.10	2181.0	$BaCl_2 \cdot 2H_2O$
	89.34	10.66	2682.7		90.54	9.46	2311.1		91.58	8.42	2127.4	
	87.60	12.40	2623.4		86.71	13.29	2308.2		88.19	11.81	2045.5	
	85.31	14.69	2536.2		84.41	15.59	2241.3		86.16	13.84	1981.9	
	84.50	16.50	2608.1		80.13	19.87	2590.0		82.72	17.28	1940.0	
	83.20	16.80	2895.3		78.26	21.74	2699.0		73.90	26.10	2561.0	
	80.80	19.20	3860.0		73.75	26.25	3512.2		71.90	29.10	3429.8	
	63.67	36.33	6283.4		51.06	48.94	5531.9		50.63	49.37	3945.1	
	52.51	47.50	7458.0		25.31	74.69	5560.0	$Ba(NO_3)_2$	32.20	67.80	4150.0	$Ba(NO_3)_2$
	27.59	72.41	8144.4	$Ba(NO_3)_2$	22.48	77.52	4942.3		23.41	76.59	3953.9	
	15.58	84.42	7119.4		13.15	86.85	4479.3		4.80	95.20	2172.9	
	13.84	86.16	7060.5		8.46	92.54	3741.4		2.13	97.87	1653.1	
	6.00	94.00	4848.1		1.21	98.79	1669.7		–	100	264.0	$Ca(NO_3)_2$
	0.47	99.53	1682.2		–	100	479.1	$Ca(NO_3)_2 \cdot 4H_2O$				
$Ca(NO_3)_2-H_2O$	–	100	703.4	$Ca(NO_3)_2 \cdot 4H_2O$								

TABLE 9

Polytherm of the system $BaCl_2-Ca(NO_3)_2-H_2O$ (diagonal section) from the temperature of complete solidification up to + 60° (Figs. 5 and 6)

Salt systems investigated	Temperature	Content of salts and water (in weight %)			Content of salts (in mole %)		Moles water per 100 moles anhydrous salts	Bottom phases
		$BaCl_2$	$Ca(NO_3)_2$	H_2O	$BaCl_2$	$Ca(NO_3)_2$		
				Boundary line of ice				
$BaCl_2-H_2O$	− 7.6°	23.50	−	76.50	100	−	3724.3	Ice + $BaCl_2 \cdot 2H_2O$
$BaCl_2-Ca(NO_3)_2-H_2O$	− 7.7	23.15	1.15	75.70	94.16	5.84	3564.7	
	− 8.0	23.15	1.53	75.32	92.70	7.30	3483.5	
	− 8.3	23.00	1.32	75.08	90.49	9.51	3409.9	Ice + $BaCl_2 \cdot 2H_2O$ + $Ba(NO_3)_2$
	− 7.6	19.20	1.97	78.91	88.47	11.53	4215.6	Ice + $Ba(NO_3)_2$
	− 5.0	12.50	2.27	85.23	80.00	20.00	7683.3	
	− 3.6	4.00	3.36	92.64	51.56	48.44	12947.6	
	− 2.2	2.39	4.10	93.51	31.51	68.49	14222.3	
	− 2.0	1.50	4.93	93.57	19.36	80.64	13957.3	
	− 5.0	1.25	5.93	92.82	14.26	85.74	12216.0	
	− 3.0	1.00	7.43	91.57	9.39	90.61	10166.2	
	− 4.5	0.80	9.92	89.28	5.97	94.03	7702.5	
	− 6.0	0.60	14.91	84.49	3.10	96.90	5000.1	
	−15.0	0.08	34.97	64.95	0.17	99.83	1682.8	
$Ca(NO_3)_2-H_2O$	−28.5	−	42.00	58.00	−	100	1335.4	Ice + $Ca(NO_3)_2 \cdot 4H_2O$
				Solutions saturated with two salts				
$BaCl_2-Ca(NO_3)_2-H_2O$	20	27.10	4.42	68.48	82.90	17.10	2419.3	$BaCl_2 \cdot 2H_2O$ + $Ba(NO_3)_2$
	40	28.80	5.24	65.95	81.40	18.60	2153.0	
	60	30.70	6.50	62.80	78.70	21.30	1904.1	
	− 8.3	23.00	1.92	75.08	90.49	9.51	3409.9	Ice + $BaCl_2 \cdot 2H_2O$ + $Ba(NO_3)_2$

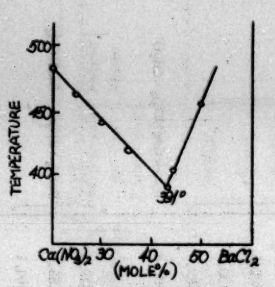

Fig. 7. Melting point diagram of system $BaCl_2-Ca(NO_3)_2$.

TABLE 10

Temperature	Content of salts (mole %)	
	$BaCl_2$	$Ca(NO_3)_2$
484°	20	80
460	25	75
440	30	70
420	35	65
402	40	60
395	43	57
403	45	55
456	50	50

Note: E at 391° and 49 weight % or 43.5 mole % $BaCl_2$.

3. System $BaCl_2-Ca(NO_3)_2-H_2O$ (diagonal section) was first studied by us, both by the solubility method and by the melting point method. Solubility data up to 120° are detailed in Tables 7 to 9, and plotted in Figs. 5a, 5b and 6. Melting point data of the system $BaCl_2-Ca(NO_3)_2$ are given in Table 10 and Fig. 7.

In order to ascertain the form of the hydrate of calcium nitrate present in the lower phases at various temperatures, reference data were used [7, 3].

The sharp decrease in the solubility of barium nitrate observed in the system $BaCl_2-Ca(NO_3)_2-H_2O$ is due to the salting out action of the strongly hydrated calcium chloride.

As in the system $CaCl_2-Ba(NO_3)_2-H_2O$, the eutonic point could not be experimentally determined because the crystallization of barium nitrate closely approaches the calcium nitrate ordinate.

In Fig. 5,B and 6, the polytherm of the system is hypothetically exterpolated until it connects the eutectic point of the anhydrous system $BaCl_2-Ca(NO_3)_2$ whose fusibility was investigated by one of us [Table 10, Fig. 7].

Fig. 5b is a representation on a reduced scale of the polytherm of the system $BaCl_2-Ca(NO_3)_2-H_2O$ from complete solidification up to the melts. The position of the triple equilibrium point E_1 [$BaCl_2-Ca(NO_3)_2-Ba(NO_3)_2-H_2O$] is shown hypothetically. We see that at 391° in the absence of water in the melts, the equilibrium of the reaction $CaCl_2 + Ba(NO_3)_2 \rightleftharpoons Ca(NO_3)_2 + BaCl_2$ is shifted to the right, and the system $BaCl_2-Ca(NO_3)_2$ is a stable diagonal system. With falling temperature in presence of water, the reaction proceeds in the reverse direction, i. e., in that of formation of $Ba(NO_3)_2$. These facts show that the direction of the exchange reaction of our salts in melts is opposite to that in solutions.

In Fig. 6 the isotherms, represented in molar percentages of anhydrous salts against the number of moles of water corresponding to 100 moles of total anhydrous salts, are closely crowded at the $Ca(NO_3)_2$ ordinate. The triple eutonic probably has the composition of 99.91% $Ca(NO_3)_2$, 0.09% $BaCl_2$ and 800 moles water.

A comparison of the two diagonal sections that we have studied, $CaCl_2-Ba(NO_3)_2-H_2O$ and $BaCl_2-Ca(NO_3)_2-H_2O$, is of considerable interest. These sections intersect in the space along the line joining the "conversion point" (50 mole % salts) with the water vertex. This "conversion line" is represented by a broken line in Figs. 3 and 5 a after recalculation of 50% (molecular) salts into weight percentages, and in Figs. 4 and 6. On superposing the respective triangles (Figs. 3 and 5 a) and the rectangular diagrams (Figs. 4 and 6) the distances between the isotherms on the branch of barium nitrate along the broken "conversion line" are found to be equal. This may serve as confirmation of the correctness of the diagrams that we plotted for the systems $CaCl_2-Ba(NO_3)_2-H_2O$ and $BaCl_2-Ca(NO_3)_2-H_2O$.

SUMMARY

1. A study was made of the systems $BaCl_2-Ba(NO_3)_2-H_2O$, $CaCl_2-Ba(NO_3)_2-H_2O$ and $BaCl_2-Ca(NO_3)_2-H_2O$ from the temperatures of complete solidification up to +60°. Results are presented in the form of the 20, 40 and 60° solubility isotherms. The boundaries of the ice fields were also established.

2. The influence of calcium chloride and nitrate in promoting the separation of barium nitrate was established.

3. A graphical comparison was made of the solubility diagrams of the diagonal sections of $CaCl_2-Ba(NO_3)_2-H_2O$ and $BaCl_2-Ca(NO_3)_2-H_2O$, and the complete identity of the isotherms on both diagrams in the region of the barium nitrate field was established.

4. It was established that in the reciprocal system of the chlorides and nitrates of barium and calcium, the direction of the exchange reaction in presence of water is opposite to that in the absence of water.

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TERNARY RECIPROCAL SYSTEM OF THE MOLYBDATES AND FLUORIDES OF SODIUM AND POTASSIUM

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In previous investigations of the system of the molybdates and chlorides of sodium and potassium, the presence was established of two complexes, melting with decomposition, between the molybdates of sodium and potassium of 1:1 and 1:2 compositions, which separate spontaneously from the melts. It was also established that, due to the considerable complex formation and, apparently, the small standard heat of the exchange reaction, the melting point diagram of the system Na, K||Cl, MoO_4 constitutes a system of a new adiagonal type with an internal phase triangle and consequently an internal triple eutectic point.

In the present paper data are presented of an investigation of the system Na, K||F, MoO_4. Replacement of the chlorine ion by the fluorine ion gave extremely interesting results which clearly demonstrate the difference in the chemical behavior of fluorine and chlorine. The marked tendency toward complex formation in the chloride-molybdate system predominated over the double decomposition. In the fluoride-molybdate system, by contrast, the double decomposition and the shift of the reaction in the direction of $Na_2F_2-K_2MoO_4$ predominates over the complex formation. The stable diagonal of $Na_2F_2-K_2MoO_4$ is represented by a system with a eutectic change at 688°.

EXPERIMENTAL

The investigation was carried out by the visual-polythermic method. Temperatures were measured with a Pt–Pt, Pd, Au thermocouple using a mirror millivoltmeter.

All results are expressed in molar percentages. Starting substances: chemically pure sodium fluoride with melting point 990°; potassium fluoride was prepared by dissolving chemically pure $KHCO_3$ in twice-distilled hydrofluoric acid and was dehydrated by slow heating in a platinum dish with continuous stirring. Melting point of potassium fluoride 858°. Sodium and potassium molybdates were prepared by fusing the respective carbonates with freshly prepared MoO_3 taken in the stoichiometric ratios. Melting point of Na_2MoO_4 688° and of K_2MoO_4 926°. The experimental data are set forth in tables in shortened form.

Binary systems. 1. $K_2F_2-Na_2F_2$ has been studied by many authors [2,3]. The eutectic corresponds to 710° and 60% K_2F_2 (Fig. 1, 1).

2. $Na_2MoO_4-Na_2F_2$ was investigated by us. A compound melting with decomposition is formed, with apparently 3:1 composition, i.e., $3Na_2MoO_4 \cdot Na_2F_2$. Eutectic at 611° and 11% Na_2F_2, and transition point at 666° and 21.5% Na_2F_2 (Fig. 1, 2; Table 1).

3. $K_2F_2-K_2MoO_4$: a compound with the composition $K_2F_2 \cdot K_2MoO_4$ exists, melting without decomposition at 754°. Eutectics: 722° and 45% K_2MoO_4; 745° and 72% K_2MoO_4 (Fig. 1, 3; Table 1).

4. $Na_2MoO_4-K_2MoO_4$ was investigated previously [4,5]. According to the published results, two compounds with apparently the following compositions are formed in the system: $Na_2MoO_4 \cdot K_2MoO_4$ and $Na_2MoO_4 \cdot 2K_2MoO_4$. Eutectic point at 667° and 19% K_2MoO_4 and two transition points at 686° and 37% K_2MoO_4 and 737° and 54% K_2MoO_4 (Fig. 1, 4; Table 1).

The reciprocal system Na, K||F, MoO_4. 24 internal sections (Figs. 2 to 4; Table 2; Fig. 5) were investigated, two of which were diagonal sections (Fig. 1, 5 and 6; Tables 1 and 4). Fig. 7 is a projection of the curves of common crystallization on to the $K_2MoO_4-K_2F_2$ side, with the aid of which the invariant points in the system were determined and the isothermal points on the curves of common crystallization were found. The surface of crystallization consists of 8 fields (Fig. 6); 4 of these belong to components and 4 to complexes of the sides. Field D_I corresponds to the complex $3Na_2MoO_4 \cdot Na_2F_2$; it has the form of a triangle terminating in the transition point R 595° at which the complex breaks down; it does not participate in the triangulation of the system. Fields D_{II} and D_{III} belong to complexes of sodium and potassium molybdates. Field D_{IV} corresponds to the compound $2K_2MoO_4 \cdot K_2F_2$. As seen from the configuation of the

TABLE 1

$K_2F_2-K_2MoO_4$		$K_2F_2-Na_2MoO_4$		$K_2MoO_4-Na_2F_2$		$Na_2MoO_4-Na_2F_2$		$Na_2MoO_4-K_2MoO_4$	
% K_2MoO_4	Temperature	% Na_2MoO_4	Temperature	% Na_2F_2	Temperature	% Na_2F_2	Temperature	% K_2MoO_4	Temperature
0	858°	0	858°	0	926°	0	688°	0	688°
4	848	20	716	10	846	4	660	8	686
10	833	24	682	15	806	8	628	13	684
15	822	29	683	20	774	12	624	16	681
18	812	33	714	24	746	16	644	19	679
24	790	37	750	28	722	20	662	22	677
28	780	41	762	32	694	24	690	28	679
32	770	45	776	36	712	28	722	34	684
36	756	50	786	40	742	32	760	37	688
40	742	54	788	44	757	50	852	40	697
43	728	58	788	48	776	52	858	46	715
46	724	62	780	54	800	100	990	54	736
50	734	66	768	58	818	–	–	55	743
54	743	70	750	62	836	–	–	58	760
57	748	76	710	70	870	–	–	62	775
62	750	80	666	100	990	–	–	66	788
66	754	84	625	–	–	–	–	70	806
70	750	86	618	–	–	–	–	74	821
74	770	89	608	–	–	–	–	82	856
78	804	90	606	–	–	–	–	90	884
100	926	100	688	–	–	–	–	100	926
Points of intersection:		Points of intersection:		Points of intersection:		Points of intersection:		Points of intersection:	
722° and 45% K_2MoO_4. 745° and 72.5% K_2MoO_4.		688° and 27% Na_2MoO_4. 618° and 85% Na_2MoO_4. 598° and 89.5% Na_2MoO_4.		688° and 33% Na_2F_2.		611° and 11% Na_2F_2. 660° and 21.5% Na_2F_2.		667° and 19% K_2MoO_4. 686° and 37% K_2MoO_4. 737° and 54% K_2MoO_4.	

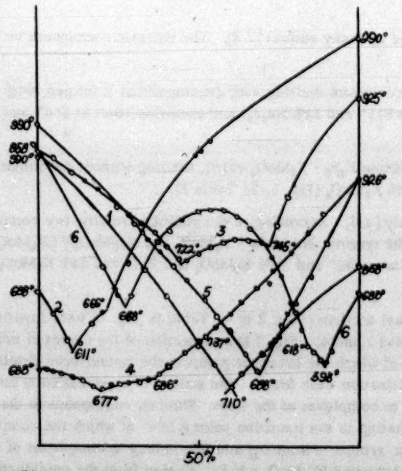

Fig. 1. Binary systems and diagonal sections of the system Na,K‖F, MoO_4. 1-$K_2F_2-Na_2F_2$, 2-$Na_2MoO_4-Na_2F_2$, 3-$K_2F_2-K_2MoO_4$, 4-$Na_2MoO_4-K_2MoO_4$, 5-$Na_2F_2-K_2MoO_4$, 6-$K_2F_2-Na_2MoO_4$.

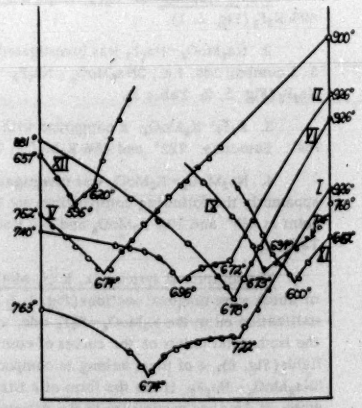

Fig. 2. Internal sections of the system.

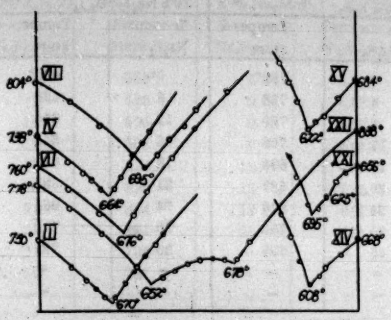

Fig. 3. Internal sections of the system.

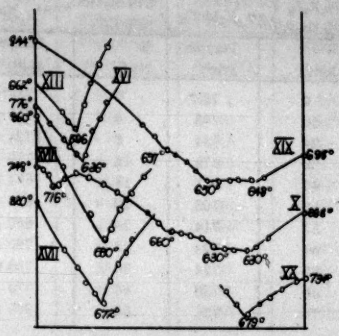

Fig. 4. Internal sections of the system.

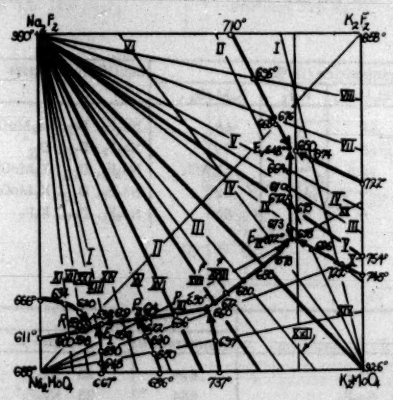

Fig. 5. Arrangement of the sections and triangulation of the system Na, K || F, MoO_4. Explanation in text.

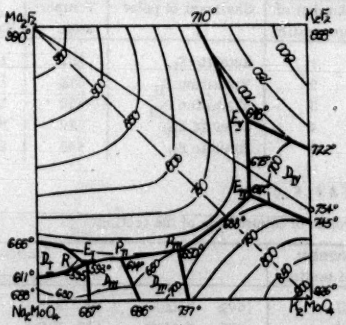

Fig. 6. Projection of the surface of crystallization of the system Na, K || F, MoO_4 onto the square of composition. Explanation in text.

field, this compound does not break down even inside the system. Comparison with the system Na, K || Cl, MoO_4 [1] shows that the fluoride system differs in that exchange reaction dominates over complex--forming reactions (Fig. 6). The system Na, K || F, MoO_4 contains 4 triangulating secants which divide the square of the system into 5 phase triangles. It is interesting to note that all the secants originate at the apex of sodium fluoride which is the pole of a four-ray triangulating star. The phase field of crystallization has a linear character and consists of 5 invariant points, 3 of which are eutectics (Fig. 6). The composition and temperature of the invariant points are detailed in Table 3. The interactions between the components of the system may be represented by the following equations:

TABLE 2

Section I		Section V		Section IX		Section XI	
75% K_2F_2, 25% Na_2F_2 → K_2MoO_4		67% K_2MoO_4, 33% K_2F_2 → Na_2F_2		74% K_2MoO_4, 26% K_2F_2 → Na_2F_2		90% K_2MoO_4, 10% Na_2MoO_4 → Na_2F_2	
% K_2MoO_4	Temperature	% Na_2F_2	Temperature	% Na_2F_2	Temperature	% Na_2F_2	Temperature
0	763°	0	752°	0	768°	0	662°
30	703	4	738	4	738	8	626
34	684	8	724	8	720	12	604
38	679	12	710	12	706	15	610
42	698	16	694	16	698	18	624
46	708	20	680	20	687	21	638
50	714	24	680	24	676	24	664
54	724	32	720	35	750	30	710
62	724	36	738	45	795	33	728
66	728	44	778	–	–	–	–
70	736	50	800	–	–	–	–
Points of intersection: 674° and 36.5% K_2MoO_4, 722° and 68% K_2MoO_4.		Points of intersection: 674° and 22.5% Na_2F_2.		Points of intersection: 724° and 5% Na_2F_2, 674° and 24% Na_2F_2.		Points of intersection: 360° and 13% Na_2F_2, 634° and 20.5% Na_2F_2.	

TABLE 3

Number of preparation	Character of point	Temperature	Composition (in %)				Equilibrium phases
			Na_2F_2	Na_2MoO_4	K_2F_2	K_2MoO_4	
1	Eutectic E_I	593°	14	68	–	18	Na_2F_2, D_{II}, Na_2MoO_4
2	Transition P_{II}	614	15	55	–	30	Na_2F_2, D_{III}, D_{II}
3	Transition P_{III}	650	18	30.5	–	51.5	Na_2F_2, D_{III}, K_2MoO_4
4	Eutectic E_{IV}	672	22	–	16	62	Na_2F_2, D_{IV}, K_2MoO_4
5	Eutectic E_V	648	23	–	42	35	Na_2F_2, D_{IV}, K_2F_2

TABLE 4

Points of intersection of the sections

Number of sections	Sections	Intersections	
		Temperature	Mole-%
III	(60% K_2MoO_4 + 40% K_2F_2) → Na_2F_2	670°	23 Na_2F_2
IV	(53% K_2MoO_4 + 47% K_2F_2) → Na_2F_2	664	23 Na_2F_2
VI	(75% Na_2F_2 + 25% K_2F_2) → K_2MoO_4	678	66.5 K_2MoO_4
VII	(65% K_2F_2 + 35% K_2MoO_4) → Na_2F_2	676	27 Na_2F_2
VIII	(80% K_2F_2 + 20% K_2MoO_4) → Na_2F_2	695	34.5 Na_2F_2
XIII	(77.5% Na_2MoO_4 + 22.5% K_2MoO_4) → Na_2F_2	598	15.5 Na_2F_2
XIV	(70% Na_2MoO_4 + 30% K_2MoO_4) → Na_2F_2	608	16 Na_2F_2
XV	(60% Na_2MoO_4 + 40% K_2MoO_4) → Na_2F_2	622	16 Na_2F_2
XVI	(50% K_2MoO_4 + 50% Na_2MoO_4) → Na_2F_2	636	17 Na_2F_2
XVII	(75% K_2MoO_4 + 25% Na_2MoO_4) → Na_2F_2	672	24 Na_2F_2
XVIII	(85% K_2MoO_4 + 15% Na_2MoO_4) → Na_2F_2	680	26 Na_2F_2
XX	(50% K_2MoO_4 + 50% K_2F_2) → Na_2MoO_4	679	22.5 Na_2MoO_4

Section XII		Section XXI		Section XXII		Section XIX	
85% Na_2MoO_4, 15% K_2MoO_4 → Na_2F_2		20% K_2MoO_4, 80% Na_2MoO_4 → Na_2F_2		79% K_2F_2, 21% Na_2F_2 → 79% K_2MoO_4, 21% Na_2MoO_4		83% K_2MoO_4, 17% Na_2MoO_4 → Na_2MoO_4	
% Na_2F_2	Temperature	% Na_2F_2	Temperature	Percent of Mixture	Temperature	% Na_2MoO_4	Temperature
0	656°	0	656°	0	778°	0	845°
5	628	3	650	10	750	40	727
10	606	6	640	20	716	44	710
12	595	9	618	30	673	49	694
15	604	12	607	38	659	52	686
18	620	15	612	42	668	60	662
21	654	18	645	46	676	64	650
24	684	21	668	50	682	68	650
27	708	—	—	58	682	75	650
30	737	—	—	62	683	80	650
—	—	—	—	71	700	85	654
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
Points of intersection: 595° and 12% Na_2F_2, 620° and 18% Na_2F_2.		Points of intersection: 620° and 8.5% Na_2F_2, 595° and 14% Na_2F_2.		Points of intersection: 650° and 30% mixture, 682° and 62% mixture.		Points of intersection: 697° and 47% Na_2MoO_4, 650° and 64% Na_2MoO_4, 648° and 81.5% Na_2MoO_4.	

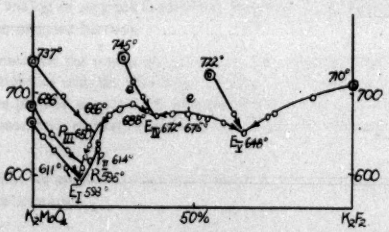

Fig. 7. Projection of the curves of common crystallization onto the $K_2MoO_4-K_2F_2$ side.

$$2Na_2MoO_4 + K_2F_2 = Na_2MoO_4 \cdot K_2MoO_4 + Na_2F_2,$$

$$3Na_2MoO_4 + 2K_2F_2 = 2Na_2F_2 + 2K_2MoO_4 \cdot Na_2MoO_4,$$

$$Na_2MoO_4 + K_2F_2 = K_2MoO_4 + Na_2F_2,$$

$$3K_2F_2 + 2Na_2MoO_4 = 2Na_2F_2 + 2K_2MoO_4 \cdot K_2F_2.$$

SUMMARY

1. A study was made of the melting point diagram of the ternary reciprocal system of the fluorides and molybdates of sodium and potassium Na, K || F, MoO_4, which comprises 8 fields of crystallization converging at 5 invariant points of which 3 are eutectic.

2. In the binary system of sodium fluorides and molybdates the existence was established of a compound, melting with decomposition, with the probable composition $Na_2F_2 \cdot 3Na_2MoO_4$, which peters out in the ternary reciprocal system and therefore has no influence at all upon the triangulation of the system.

3. The system K_2F_2-K_2MoO_4 contains a compound, melting without decomposition, with the composition $K_2F_2 \cdot 2K_2MoO_4$; this is also stable in the ternary system.

4. The two complexes between sodium and potassium molybdates, previously established by us, are represented in the present system by extremely characteristic fields.

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SYNTHESIS AND PROPERTIES OF NIOBIUM BRONZES

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Compounds analogous to the tungsten bronzes have not been reported in the literature for elements of the transition groups of Mendeleev's periodic system (with exception of tungsten). Tungsten bronzes have been studied by V. I. Spitsyn [1], S. I. Sklyarenko and L. E. Levin [2] and others. Tungsten bronzes are a striking example of oxygenated salts possessing metallic properties: metallic luster, electrical conductivity, the ability to be coated with metals by electrodeposition, and so forth. Gardner and Danielson [3] studied the Hall effect and the electrical resistance of single crystals of sodium tungsten bronze Na_xWO_3 as a function of the temperature and the value of x, which may vary between 1 and 0.

The crystal structure of tungsten bronzes has been studied by C. Hagg [4]. Sodium tungsten bronze forms a cubic lattice of the pervoskite type in which a proportion of the WO_3^- ions is replaced by neutral molecules of WO_3; therefore for maintenance of the electrical neutrality of the lattice a corresponding number of sites of the positively charged (sodium) portion of the lattice remains unoccupied, and thus a defect structure of the pervoskite type is developed [5].

It is interesting to note that the electrical analog of tungsten (molybdenum) does not form compounds similar to the tungsten bronzes; this is understandable in the light of the law of secondary periodicity. In searching for elements capable of forming oxygen-containing salts with metallic properties, we made use of another law of D. I. Mendeleev, namely the diagonal analogies. Corresponding to the position in the periodic system of D. I. Mendeleev and to the atomic structure, a diagonal analog of tungsten is niobium; therefore we should expect niobium to be capable of forming compounds analogous to the tungsten bronzes.

In the present communication the results are presented of an investigation of the synthesis and properties of new compounds of tetravalent niobium with the alkali and alkaline earth metals which possess the above-noted metallic properties, and we therefore propose to call them niobium bronzes. This name is justified by the additional fact that, apart from the outward appearance, niobium bronzes resemble tungsten bronzes in respect of chemical inertness, composition and structure.

Six of the substances that we synthesizes and their characteristics are detailed in Table 1. None of them has previously been reported in the literature.

TABLE 1
Composition and properties of niobium bronzes

Empirical formula	Color of compound	Specific gravity at 20°C	Type of crystalline lattice	Temperature of experiment
Li_2NbO_3	Lustrous grey	4.30	Not established	1200°
$Na_4Nb_3O_8$	Pinkish	4.85	Same	1100
$K_2Nb_2O_5$	Metallic grey	3.56	Same	950
$CaNbO_3$	Dark-blue	4.47	Pervoskite	1350
$SrNbO_3$	Blue-violet	5.11	Same	1300
$BaNbO_3$	Red-violet	5.20	Not established	1250

EXPERIMENTAL

1. Starting preparations. The niobium starting substance was niobium dioxide, prepared by reduction with hydrogen of chemically pure niobium pentoxide free from tantalum and titanium. The niobium pentoxide was purified as described previously [6].

Lithium oxide was prepared by dehydration at 800°C of lithium hydroxide obtained from chemically pure lithium sulfate $Li_2SO_4 \cdot H_2O$ and barium hydroxide.

Oxides of the alkaline earth metals were obtained by calcination of the nitrates as described in the literature [7].

The sodium and potassium carbonates used in the research were chemically pure preparations. The composition of all the reagents was checked analytically as well as by magnetic methods for absence of impurities. We regarded para-magnetic impurities as especially harmful since magnetic investigations were included in the research plan.

2. Synthesis of niobium bronzes. For preparation of niobium bronzes we made use of the reaction of niobium dioxide with carbonates of the alkali metals or oxides of the alkaline earth metals. Experiments on the preparation of niobium bronzes of lithium and the alkaline earth metals were carried out at 1200-1350° in a crucible vacuum electric furnace with a tungsten heating element. A weighed amount of the oxide of the alkaline earth metal (or lithium oxide) was mixed in an agate mortar with the calculated amount of niobium dioxide, and this mixture was transferred to a beryllium oxide crucible. The crucible was placed in a TVV-2 vacuum furnace from which the air was pumped out to a pressure of $2 \cdot 10^{-4}$ mm, at first at room temperature and later at 400°. The temperature was gradually raised to the level specified in Table 1, previously established for each of the substances that we synthesized. After a period of 1-2 hours, the current was switched off and the furnace cooled to room temperature; only after this was air introduced into the system, and the cake of sintered crystals of niobium bronze was extracted from the crucible.

Preparation of niobium bronzes of sodium (or potassium) requires a lower temperature, and therefore the reaction between sodium (potassium) carbonate and niobium dioxide was conducted in a tubular electric furnace with a silit heating element.

The thoroughly mixed starting substances were placed in a small beryllium oxide boat which was slid into a long quartz tube sealed at one end. The other end of the tube was connected by a water-cooled ground-glass fitting via a three-way piece with a vacuum pump and a pressure gage. At first the air was pumped out of the whole system to a pressure of $2 \cdot 10^{-4}$; the pump was then disconnected and the furnace rapidly heated to 1100° (or 950° for potassium).

The amount of carbon dioxide evolved according to the equation

$$2Na_2CO_3 + 3NbO_2 = Na_4Nb_3O_9 + 2CO_2.$$

could be established with the help of the pressure gage.

The duration of an experiment was 1-2 hours; at the end of the reaction the furnace was cooled, and the boat containing the niobium bronze was removed from the quartz tube, transferred to a desiccator, weighed, and analyzed.

3. Methods and results of analysis*. All the substances were analyzed for their content of niobium dioxide and metallic oxide. Niobium bronzes of the alkali metals were fused with the tenfold amount of ammonium pyrosulfate in presence of air for conversion of the niobium to the pentavalent state. After cooling, the transparent melts were treated with a saturated solution of ammonium carbonate. On heating, the solution deposited a precipitate of niobic acid which was washed on a filter with 1 N ammonium carbonate solution, dried, and calcined to constant weight.

The oxides of the alkali metals were determined in the filtrates after separation of the niobic acid. For this purpose the solution containing the sulfates of the alkali metals and ammonia was carefully evaporated on a water bath. The dry residues were then calcined to constant weight at 400-450°.

Niobium bronzes of the alkaline earth metals were fused in presence of air with fifteen times the amount of sodium carbonate. The melt on cooling was made alkaline with 0.1 N KOH solution. The carbonates of the alkaline earth metals remained in the precipitate, while the niobium went into solution. The washed precipitates of the carbonates of the alkaline earth metals were dissolved in a small excess of hydrochloric acid. The calcium from this solution was determined as oxalate, and the strontium and barium as sulfates. The filtrates, containing the niobium, were diluted with water, neutralized with hydrochloric acid until weakly acidic, and heated with constant stirring; in this way niobic acid was precipitated and was treated as in the case of niobium bronzes of the alkali metals.

In Table 2 are set forth the results of analyses of niobium bronzes.

The exact chemical formulas of niobium bronzes, like those of tungsten bronzes, cannot be determined on the basis of isolated chemical analyses.

In the calculations we took into account the whole of the niobium combined in the form of NbO_2 but in none of the analyses was the sum of the basic oxide and the acidic NbO_2 equal to 100. This may be explained by assuming that some proportion of the niobium remained bound in the form of niobium pentoxide.

* With participation of V. A. Samarina.

A complete solution of the problem of the composition and structure of niobium bronzes may be expected after detailed X-ray investigations.

TABLE 2
Analysis of niobium bronzes

Bronze	Composition of bronze				Atomic ratio of M : Nb	Approximate chemical formula
	$M_2O(MO)$, %		NbO_2, %			
	Found	Calculated	Found	Calculated		
Lithium	15.91	19.25	78.38	80.75	1.70	Li_2NbO_3
Sodium	19.93	24.80	78.09	75.20	1.24	$Na_4Nb_3O_8$
Potassium	26.79	24.40	68.09	75.60	1.03	$K_2Nb_2O_5$
Calcium	27.48	30.88	70.78	69.12	0.87	$CaNbO_3$
Strontium	44.00	45.04	55.60	54.96	0.90	$SrNbO_3$
Barium	45.05	53.20	49.70	46.80	0.75	$BaNbO_3$

TABLE 3
Magnetic susceptibility of niobium bronzes

Substance	Magnetic molecular moment in Bohr magnetons at various temperatures		
	+ 17°C	−67°C	−195°C
NbO_2	0.26	0.20	0.15
Li_2NbO_3	0.20	0.18	0.14
$K_2Nb_2O_5$	0.54	0.33	0.25
$Na_4Nb_3O_8$	0.46	0.37	0.27
$CaNbO_3$	0.40	0.31	0.19
$SrNbO_3$	0.37	0.30	0.20
$BaNbO_3$	0.34	0.23	0.14

TABLE 4
Magnetic moments of ions of the higher transition elements

Number of electrons	Ion	Magnetic moment in Bohr magnetons	
		theoretical	experimental
1	Nb^{4+}	1.73	0.19−0.43
3	Mo^{3+}, Re^{4+}	3.87	3.7−3.2
4	Re^{3+}	4.90	0.4
5	Ru^{3+}, Ir^{3+}	5.92	2.09−0.11
6	Os^{2+}	4.90	0.27−0.5
8	Pd^{2+}	2.83	0.07−0.11
9	Ag^{2+}	1.73	1.73

TABLE 5
Electrical resistance of a powder under various pressures (Temperature 18°)

Pressure $P \cdot 10^3$ (in kg/cm²)	Electrical resistance Ω
0.80	0.00350
1.15	0.00325
1.72	0.00275
2.30	0.00245
2.90	0.00155
3.45	0.00105
5.17	0.00105

Note: Length of pellet at final pressure 7 mm; cross-sectional area 23 mm².

4. Magnetic investigations of niobium bronzes. Data for the magnetic susceptibility of niobium dioxide are extremely scanty. Brauer [8] determined the molar susceptibilities in the system Nb−O between Nb and Nb_2O_5. Their change with composition is consistent with the phase boundaries of the system as found by X-ray ray measurements [9].

Brauer gives the following value for the molar magnetic moment: $\mu_{eff.} = 0.43$ Bohr magneton. If it is assumed that the magnetic spin of the ground state $^2D_{3/2}$ of the Nb^{4+} ion is the sole source of paramagnetism, the low value of the magnetic moment in comparison with the theoretical value is unexpected; the latter should be 1.73 Bohr magnetons. Brauer does not explain this discrepancy. We carried out measurements of the magnetic susceptibility of niobium dioxide and niobium bronzes of the alkali and alkaline earth metals, using the cylinder method [10] with a small laboratory electromagnet at a field intensity of 3,500 to 4,500 oersteds. Results of measurements are set forth in Table 3, which includes for comparison our date for the magnetic moment of niobium dioxide.

As we see from the data of Table 3, our values of the magnetic moment of niobium dioxide are even lower than those of Brauer. This may be due to the higher purity of the NbO_2 at out disposal

For none of the niobium bronzes was agreement found between the theoretical and experimental values of the magnetic moment.

It must be mentioned that for the higher transition elements, i.e., for elements of the even series of the 5th and 6th periods of the periodic system of Mendeleev, these values do not agree in the majority of cases (Table 4).

This might be accounted for on the assumption that due to the greater charge of the nucleus of the atom in ions of the higher transition elements, the bonds between the spin and the orbital magnetic moments become stronger than in the transition elements of the 4th period, and therefore Stoner's formula $\mu_{eff.} = \sqrt{n(n+2)}$, where n is the number of unpaired electrons, is unsuitable for calculation of the magnetic moments of the ions.

5. Specific electrical resistance of calcium-niobium bronze $CaNbO_3$. The electrical resistance of $CaNbO_3$ powder was measured on a Thomson bridge of the MT-5 type. During measurement the powder was subjected to a pressure of 0 to 5000 kg/cm^2 in a hydraulic press. Results are presented in Table 5.

The specific electrical resistance can be calculated from the above data. Thus, at 18° and pressures of 3.45 to 5.17 t/cm^2 it was equal to $0.35 \cdot 10^{-3}$ Ω cm. Consequently, calcium niobium bronze possesses electronic (metallic) conductivity.

SUMMARY

1. The preparation was realized for the first time of niobium bronzes with variable compositions represented by the following approximate formulas:

Li_2NbO_3; $K_2Nb_2O_5$; $Na_4Nb_3O_9$; $CaNbO_3$; $SrNbO_3$ and $BaNbO_3$.

2. The specific gravities of niobium bronzes were determined by the pycnometric method.

3. The molecular magnetic moments of niobium bronzes were determined. It was shown that for the higher transition elements the formula of Stoner is unsuitable for calculation of magnetic moments.

4. The specific electrical resistance of calcium niobium bronze was determined; the resistance is of the same order of magnitude as that of a first-order conductor.

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THE SOLUBILITY OF SILVER BROMATE IN AQUEOUS SOLUTIONS OF POTASSIUM BROMATE AND SODIUM NITRATE

THE INFLUENCE OF ELECTROLYTES WITH LIKE IONS UPON THE SOLUBILITY AND SOLUBILITY PRODUCT OF THE PRECIPITATE

Yu. L. Lelchuk, L. V. Surnina and V. I. Barkhamova

The present communication is a continuation of our publications on the influence of electrolytes of various types upon the solubility and solubility product of precipitated silver bromate [1-3], and its objective is the clarification of the general laws of the influence of electrolytes of various types upon the solubility and solubility product of precipitates in the absence of a definite chemical interaction between the precipitates and the electrolytes.

In the present investigation we studied the effect of an electrolyte containing an ion also present in the precipitate upon the solubility of precipitated silver bromate. For this purpose we studied the solubility in the system $AgBrO_3-KBrO_3-H_2O$. Since as a rule, in systems of analytical importance electrolytes that do not contain a common ion are present in addition to the precipitant, we undertook a study of the solubility of the precipitate in the simultaneous presence in the solution of an electrolyte containing a common ion and of an electrolyte not containing an ion common to the precipitate. For this purpose we studied the solubility in the four-component system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ with potassium bromate concentrations of 0.001, 0.01 and 0.1 M, and sodium nitrate concentrations of 0.001 to 1 M.

For comparative evaluation of the contribution of an electrolyte of the I–I type, lacking ions common to the precipitate, to the rise in solubility of the precipitate and of the extent of the fall in solubility of precipitated $AgBrO_3$ under the influence of a I–I type of electrolyte containing an ion also present in the precipitate when both are simultaneously present in the solution, we compared our earlier data for the system $AgBrO_3-NaNO_3-H_2O$ [1] with data for the solubility in the systems $AgBrO_3-KBrO_3-NaNO_3-H_2O$ and $AgBrO_3-KBrO_3-H_2O$.

TABLE 1

Solubility of $AgBrO_3$ in aqueous solutions of $KBrO_3$

$KBrO_3$ (M)	Solubility of $AgBrO_3$ (M)			
	experiment 1	experiment 2	experiment 3	mean
0.000	$8.244 \cdot 10^{-3}$	$8.252 \cdot 10^{-3}$	$8.249 \cdot 10^{-3}$	$8.25 \cdot 10^{-3}$
0.001	$7.25 \cdot 10^{-3}$	$7.33 \cdot 10^{-3}$	$7.37 \cdot 10^{-3}$	$7.32 \cdot 10^{-3}$
0.003	$5.29 \cdot 10^{-3}$	$5.31 \cdot 10^{-5}$	$5.28 \cdot 10^{-3}$	$5.29 \cdot 10^{-3}$
0.010	$3.98 \cdot 10^{-3}$	$4.01 \cdot 10^{-3}$	$3.97 \cdot 10^{-3}$	$3.99 \cdot 10^{-3}$
0.030	$2.48 \cdot 10^{-3}$	$2.47 \cdot 10^{-3}$	$2.52 \cdot 10^{-3}$	$2.49 \cdot 10^{-3}$
0.100	$9.75 \cdot 10^{-4}$	$1.10 \cdot 10^{-3}$	$1.10 \cdot 10^{-3}$	$1.06 \cdot 10^{-3}$
0.300	$7.00 \cdot 10^{-4}$	$7.12 \cdot 10^{-4}$	$6.96 \cdot 10^{-4}$	$7.03 \cdot 10^{-4}$

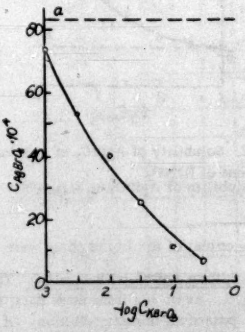

Fig. 1. Solubility of $AgBrO_3$ in aqueous solutions of $KBrO_3$.
a) Solubility of $AgBrO_3$ in water.

Starting substances and experimental technique. Pure potassium bromate was prepared from potassium hydroxide and bromine by Ilin's method [4]. It conformed to the OST* requirements for purity of $KBrO_3$ [5]. Sodium nitrate was obtained from the twice-recrystallized commercial Russian material by Lait's method as described by Karyakin [4]. Silver bromate was prepared from silver nitrate and potassium bromate. Details of its preparation have been described earlier [2]. All the solutions of sodium nitrate were obtained by appropriate dilution of 1 M $NaNO_3$ solution; those of potassium bromate were prepared by dilution of 0.3 M $KBrO_3$ solution. The solutions were prepared and diluted with double-distilled water stored in a bottle paraffined on the inside. Experiments on solubility determinations were performed in brown glass bottles paraffined on the inside, capacity 400-500 ml. The corked bottle, containing 1 g silver bromate and 250 ml potassium bromate solution of the appropriate concentration, was put into a water thermostat at a temperature of 25 ± 0.1°, and agitated vigorously for 8 hours. The temperature was kept constant with the help of a mercury-toluene thermoregulator.

* All-Union Standard

TABLE 2

Change of solubility product of $AgBrO_3$ in the system $AgBrO_3-KBrO_3-H_2O$

$KBrO_3$ (M)	0.000	0.001	0.003	0.010	0.030	0.100	0.300
$L_p \cdot 10^5$	6.80	6.09	4.38	5.58	8.109	10.7	21.1
$\log L_p$	−4.17	−4.21	−4.36	−4.25	−4.09	−3.97	−3.68

Note: $L_i : L_i' = 11.8$, $L_p : L_p' = 3.1$, where L_i and L_i' are the solubility of $AgBrO_3$ (in moles) in water and in 0.3 M $KBrO_3$ solution respectively; L_p and L_p' are the solubility product in water and 0.3 N $KBrO_3$ solution respectively.

TABLE 3

System $AgBrO_3-NaNO_3-H_2O$

$NaNO_3$ (M)	$AgBrO_3$ (M)	μ	γ	$L_p \cdot 10^5$	$L_a \cdot 10^5$
0.001	$8.22 \cdot 10^{-3}$	0.0092	0.901	6.76	6.08
0.003	$8.31 \cdot 10^{-3}$	0.0113	0.891	6.91	5.49
0.010	$8.50 \cdot 10^{-3}$	0.0185	0.865	7.23	5.41
0.030	$9.27 \cdot 10^{-3}$	0.0393	0.817	8.59	5.72
0.100	$1.008 \cdot 10^{-2}$	0.1101	0.731	10.2	5.44
0.300	$1.138 \cdot 10^{-2}$	0.3114	0.626	13.0	5.09
1.000	$1.48 \cdot 10^{-2}$	1.0148	0.501	21.9	5.50

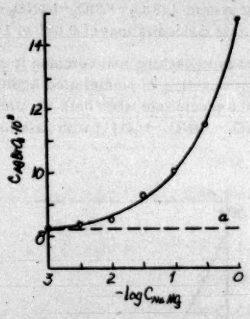

Fig. 2. Solubility of $AgBrO_3$ in aqueous solutions of $NaNO_3$. a) Solubility of $AgBrO_3$ in water.

TABLE 4

Solubility of $AgBrO_3$ in the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$. $KBrO_3$ concentration 0.001 M.

$NaNO_3$ (M)	Solubility of $AgBrO_3$ (M)			
	experiment 1	experiment 2	experiment 3	experiment 4
0.000	$7.25 \cdot 10^{-3}$	$7.39 \cdot 10^{-3}$	$7.37 \cdot 10^{-3}$	$7.32 \cdot 10^{-3}$
0.001	$7.50 \cdot 10^{-3}$	$7.58 \cdot 10^{-3}$	$7.55 \cdot 10^{-3}$	$7.54 \cdot 10^{-3}$
0.003	$7.92 \cdot 10^{-3}$	$7.88 \cdot 10^{-3}$	$7.90 \cdot 10^{-3}$	$7.90 \cdot 10^{-3}$
0.010	$8.29 \cdot 10^{-3}$	$8.16 \cdot 10^{-3}$	$8.22 \cdot 10^{-3}$	$8.22 \cdot 10^{-3}$
0.030	$8.88 \cdot 10^{-3}$	$8.82 \cdot 10^{-3}$	$8.85 \cdot 10^{-3}$	$8.85 \cdot 10^{-3}$
0.100	$9.68 \cdot 10^{-3}$	$9.68 \cdot 10^{-3}$	$9.66 \cdot 10^{-3}$	$9.67 \cdot 10^{-3}$
0.300	$1.12 \cdot 10^{-2}$	$1.12 \cdot 10^{-2}$	$1.13 \cdot 10^{-2}$	$1.12 \cdot 10^{-2}$
1.000	$1.35 \cdot 10^{-2}$	$1.36 \cdot 10^{-2}$	$1.35 \cdot 10^{-2}$	$1.35 \cdot 10^{-2}$

In the study of the solubility in the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ the necessary concentrations of sodium nitrate and potassium bromate in the liquid phase were reached by adding the requisite amount of $KBrO_3$ to a solution of sodium nitrate of the appropriate concentration. Withdrawal of liquid phase samples for analysis and determination of the silver bromate content of the liquid phase were accomplished by the previously described procedures [1].

System $AgBrO_3-KBrO_3-H_2O$. The experimental data obtained for this system are set forth in Table 1 and plotted in Fig. 1. As we see from these data, the solubility of the precipitate increases in proportion to the rise in concentration of the potassium bromate solution. Of all the concentrations of $KBrO_3$ examined, the lowest fall in solubility of $AgBrO_3$ was achieved in 0.3 M potassium bromate solution in which the solubility of the precipitate is only $7.03 \cdot 10^{-4}$ as compared with $8.25 \cdot 10^{-3}$ in water, i.e., it falls 11.8 times. The relatively good agreement of three parallel determinations of the solubility of silver bromate for each point of the system $AgBrO_3-KBrO_3-H_2O$ and the general course of the curve in Fig. 1 testify to the low probability of formation in this system of solid solutions and, in consequence, of double salts. As we know, the existence of such solid solutions and the formation of the double salt $AgBrO_3 \cdot NaBrO_3$ were established during a study of the composition of the solid phase in the system $AgBrO_3-NaBrO_3-H_2O$ at concentration of $NaBrO_3$ in the liquid phase of 22% and higher [6]. The formation of solid solutions and of the double salt $AgBrO_3 \cdot NaBrO_3$ is held by the authors to account for the impossibility of obtaining chemically pure silver bromate from concentrated solutions of sodium bromate and silver nitrate and for the great deviations in the literature data for the solubility of silver bromate in water.

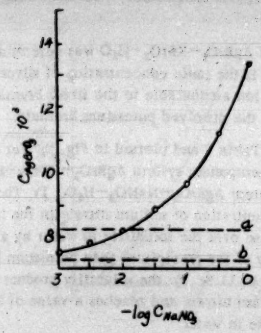

Fig. 3. Solubility of $AgBrO_3$ in the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ at $C_{KBrO_3} = 1 \cdot 10^{-3}$ M.

a) Solubility of $AgBrO_3$ in water; b) Solubility of $AgBrO_3$ in 0.001 M. $KBrO_3$.

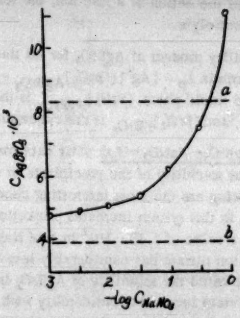

Fig. 4. Solubility of $AgBrO_3$ in the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ at $C_{KBrO_3} = 1 \cdot 10^{-2}$ M.

a) Solubility of $AgBrO_3$ in water; b) Solubility of $AgBrO_3$ in 0.01 M. $KBrO_3$.

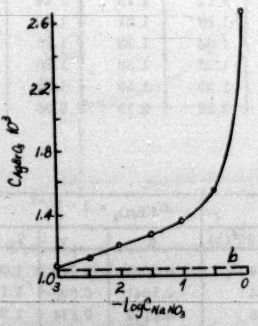

Fig. 5. Solubility of $AgBrO_3$ in the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ at $C_{KBrO_3} = 1 \cdot 10^{-1}$ M.

b) Solubility of $AgBrO_3$ in 0.1 M $KBrO_3$.

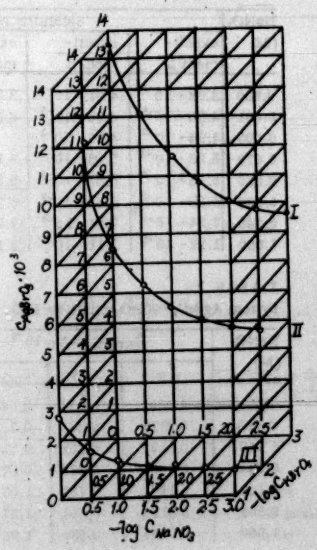

Fig. 6. Solubility of $AgBrO_3$ in the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$.

I) $C_{KBrO_3} = 1 \cdot 10^{-3}$ M., II) $C_{KBrO_3} = 1 \cdot 10^{-2}$ M., III) $C_{KBrO_3} = 1 \cdot 10^{-1}$ M.

Special interest is attached to the course of the change in solubility product of the precipitate in this system. As we see from the data of Table 2 and Fig. 7, the solubility product of $AgBrO_3$ precipitate in 0.001 and 0.003 M potassium bromate is slightly smaller than

in water. With further increase of the concentration of $KBrO_3$ in the solution, however, the solubility product proportionately increases and attains a value of $2.11 \cdot 10^{-4}$ for an 0.3 M solution of potassium bromate, i.e., 3.1 times higher than in water. Consequently, precisely as in the ternary systems previously studied by us that did not contain the same ions as in the precipitate, in which as a rule the solubility of the precipitate increased in proportion to increasing concentration of electrolyte, we find in the present ternary system that notwithstanding the fall in solubility of the precipitate under the action of a like ion, the solubility product likewise increases considerably with increasing concentration of electrolyte.

The solubility product of $AgBrO_3$ for all the point studied of the system $AgBrO_3-KBrO_3-H_2O$ was determined according to the formula $L_p = [Ag^+]([BrO_3^-]_{AgBrO_3} + [BrO_3^-]_{KBrO_3})$, where $[Ag^+]$ is the ionic concentration of silver in g-ions/liter in the liquid phase, $[BrO_3^-]_{AgBrO_3}$ is the concentration of bromate ion attributable to the silver bromate in the liquid phase, and $[BrO_3^-]_{KBrO_3}$ is the concentration of bromate ion due to the dissolved potassium bromate.

System $AgBrO_3-NaNO_3-H_2O$. Our data for this sytem are set forth in Table 3 and plotted in Fig. 2. For analysis of the data for solubility of the precipitate of silver bromate in the four-component system $AgBrO_3-KBrO_3-NaNO_3-H_2O$, the following are the most interesting conclusions in respect of the system $AgBrO_3-NaNO_3-H_2O$: 1) The solubility of $AgBrO_3$ in this system increases proportionately with the rise of concentration of sodium nitrate in the liquid phase, reaching a value of $1.48 \cdot 10^{-2}$ in 1 M $NaNO_3$ solution, i.e., an increase over the solubility in water by a factor of 1.8; thus sodium nitrate has considerably less influence upon the solubility of the precipitate than potassium bromate has; the latter lowered the solubility of $AgBrO_3$ in 0.3 M solution by a factor of 11.8; 2) the solubility product of $AgBrO_3$ in this system increases considerably with rising concentration of sodium nitrate and reaches a value of $2.19 \cdot 10^{-4}$, i.e., over 3.2 times larger than the solubility product of the precipitate in water.

TABLE 5
Solubility of $AgBrO_3$ in the system
$AgBrO_3-KBrO_3-NaNO_3-H_2O$
$KBrO_3$ concentration 0.01 M

$NaNO_3$ (M)	Solubility of $AgBrO_3$ (M)			
	experiment 1	experiment 2	experiment 3	mean
0.000	$3.98 \cdot 10^{-3}$	$4.01 \cdot 10^{-3}$	$3.97 \cdot 10^{-3}$	$3.99 \cdot 10^{-3}$
0.001	$4.75 \cdot 10^{-3}$	$4.83 \cdot 10^{-3}$	$4.87 \cdot 10^{-3}$	$4.82 \cdot 10^{-3}$
0.003	$4.94 \cdot 10^{-3}$	$4.90 \cdot 10^{-3}$	—	$4.92 \cdot 10^{-3}$
0.010	$5.03 \cdot 10^{-3}$	$5.06 \cdot 10^{-3}$	$5.16 \cdot 10^{-3}$	$5.08 \cdot 10^{-3}$
0.030	$5.43 \cdot 10^{-3}$	$5.54 \cdot 10^{-3}$	$5.50 \cdot 10^{-3}$	$5.49 \cdot 10^{-3}$
0.100	$6.39 \cdot 10^{-3}$	$6.35 \cdot 10^{-3}$	$6.37 \cdot 10^{-3}$	$6.37 \cdot 10^{-3}$
0.300	$7.54 \cdot 10^{-3}$	$7.54 \cdot 10^{-3}$	$7.58 \cdot 10^{-3}$	$7.55 \cdot 10^{-3}$
1.000	$1.12 \cdot 10^{-2}$	$1.11 \cdot 10^{-2}$	$1.13 \cdot 10^{-2}$	$1.12 \cdot 10^{-2}$

TABLE 6
Solubility of $AgBrO_3$ in the system
$AgBrO_3-KBrO_3-NaNO_3-H_2O$
$KBrO_3$ concentration 0.1 M

$NaNO_3$ (M)	Solubility of $AgBrO_3$ (M)			
	experiment 1*	experiment 2*	experiment 3*	mean*
0.000	0.98	1.10	1.10	1.06
0.001	1.09	1.05	1.08	1.07
0.003	1.12	1.13	1.14	1.13
0.010	1.18	1.21	1.20	1.20
0.030	1.24	1.23	1.26	1.24
0.100	1.33	1.33	1.36	1.34
0.300	1.52	1.50	1.53	1.52
1.000	2.62	2.78	2.68	2.69

TABLE 7
System $AgBrO_3-KBrO_3-NaNO_3-H_2O$

$NaNO_3$ (M)	$C_{KBrO_3} = 1 \cdot 10^{-3}$			$C_{KBrO_3} = 1 \cdot 10^{-2}$			$C_{KBrO_3} = 1 \cdot 10^{-1}$		
	μ	γ	$L_p \cdot 10^4$ (a)	μ	γ	$L_p \cdot 10^4$ (b)	μ	γ	$L_p \cdot 10^4$ (c)
0.001	0.0095	0.924	0.644	0.0158	0.878	0.714	0.1021	0.714	1.08
0.003	0.0119	0.885	0.703	0.0179	0.866	0.734	0.1041	0.695	1.14
0.010	0.0192	0.852	0.758	0.0251	0.846	0.766	0.1112	0.674	1.21
0.030	0.0398	0.794	0.872	0.0455	0.804	0.850	0.1312	0.644	1.25
0.100	0.1107	0.731	1.03	0.1164	0.727	1.04	0.2013	0.636	1.36
0.300	0.3122	0.634	1.37	0.3175	0.646	1.32	0.4015	0.598	1.54
1.000	1.0145	0.530	1.96	1.0212	0.482	2.37	1.1027	0.446	2.76

Notes: 1. a) $L_l' : L_l = 2.88$, $L_p' : L_p = 1.636$; b) $L_l' : L_l = 3.48$, $L_p' : L_p = 1.36$; c) $L_l' : L_l = 4.06$, $L_p' : L_p = 0.326$. 2. L_l' and L_l are the solubility of $AgBrO_3$ in 1 M $NaNO_3$ solution and in water respectively; L_p' and L_p are the solubility product of $AgBrO_3$ in 1 M $NaNO_3$ solution and in water respectively.

* The values of solubility in experiments 1, 2, and 3, and the mean values are multiplied by 10^3.

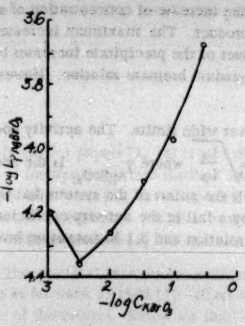

Fig. 7. Change of the solubility product of $AgBrO_3$ in the system $AgBrO_3-KBrO_3-H_2O$.

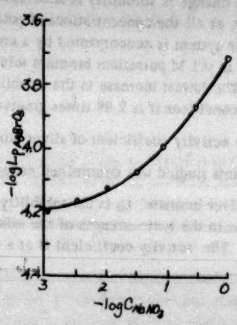

Fig. 8. Change in the solubility product of $AgBrO_3$ in the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ at $C_{KBrO_3} = 1 \cdot 10^{-3}$M.

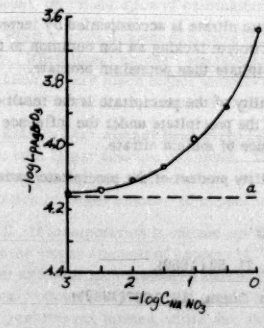

Fig. 9. Change of solubility product of $AgBrO_3$ in the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ at $C_{KBrO_3} = 1 \cdot 10^{-2}$ M.

a - corresponds to $-\log L_p$ $AgBrO_3$ in water.

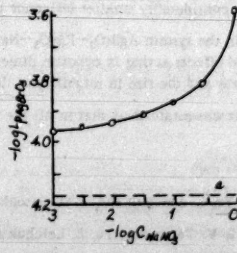

Fig. 10. Change in the solubility product of $AgBrO_3$ in the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ at $C_{KBrO_3} = 1 \cdot 10^{-1}$M.

a - corresponds to $-\log L_p$ $AgBrO_3$ in water.

System $AgBrO_3-KBrO_3-NaNO_3-H_2O$. Our experimental data for this four-component system are presented in Tables 4-7 and plotted in Figs. 3-6. At all the concentrations of potassium bromate studied, the solubility of the silver bromate precipitate increases with rising concentration of sodium nitrate. At a potassium bromate concentration of 0.001 M, the fall in solubility of the precipitate due to the presence of an ion also common to the precipitate is completely offset by a corresponding rise in solubility of the precipitate due to the presence of sodium nitrate even at a concentration of only 0.01 M $NaNO_3$. A still greater rise in concentration of sodium nitrate is accompanied by a steady increase in solubility of the precipitate. In a 1 M solution of $NaNO_3$ the solubility of silver bromate increases more than 1.6 times. With a potassium bromate concentration of 0.01 M, the fall in solubility of the precipitate due to the bromate ion is completely compensated by a corresponding rise in solubility due to sodium nitrate only at a concentration of

0.5 M. In 1 M sodium nitrate solution the solubility of the precipitate is 1.36 times higher than its solubility in water. At a potassium bromate concentration of 0.1 M, even a 1 M concentration of sodium nitrate permits the solubility of the precipitate to rise to only $2.69 \cdot 10^{-3}$ M, i.e., the solubility of the precipitate under these conditions remains 3 times smaller than its solubility in water.

The change in solubility is accompanied by a change in the solubility product of the precipitate. As we see from Figs. 8-10, at all the concentrations of potassium bromate that we studied, the increase of concentration of sodium nitrate in the system is accompanied by a constant increase in the solubility product. The maximum increase in the latter occurs in 0.1 M potassium bromate solution, in which the solubility product of the precipitate increases by a factor of 4.06. The lowest increase in the solubility product occurs in 0.001 M potassium bromate solution. However, even under these conditions it is 2.88 times greater than in water.

The activity coefficient of silver bromate in this system also varies over wide limits. The activity coefficient at all the points studied was determined according to the formula: $\gamma_{AgBrO_3} = \sqrt{\frac{L_a}{L_p}}$, where γ_{AgBrO_3} is the activity coefficient of silver bromate, L_a is the solubility product of the precipitate. At all the points of the system that were studied, an increase in the ionic strength of the solution is invariably accompanied by a fall in the activity coefficient of silver bromate. The activity coefficient is at a minimum in 1 M sodium nitrate solution and 0.1 M potassium bromate solution.

SUMMARY

1. An investigation was made of the solubility of precipitated silver bromate in the three-component system $AgBrO_3-KBrO_3-H_2O$ at concentrations of potassium bromate of 0.001 to 0.3 molar and in the four-component system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ at concentrations of potassium bromate of 0.001, 0.01 and 0.1 molar and sodium nitrate concentrations of 0.001 to 1 molar at 25°.

2. It was established that in the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ the solubility of silver bromate precipitate falls proportionately to the rise in potassium bromate concentration. At 0.3 M concentration of $KBrO_3$ the solubility of the precipitate is 11.8 times lower than its solubility in water.

3. In the system $AgBrO_3-NaNO_3-H_2O$ rising concentration of sodium nitrate is accompanied by increasing solubility of silver bromate precipitate. Sodium nitrate, however, as an electrolyte lacking an ion common to the precipitate, has a considerably smaller influence upon the solubility of the precipitate than potassium bromate.

4. In the system $AgBrO_3-KBrO_3-NaNO_3-H_2O$ the change of solubility of the precipitate is the result of two superimposed effects acting in opposite directions: the fall in solubility of the precipitate under the influence of potassium bromate and the rise in solubility of the precipitate under the influence of sodium nitrate.

5. It was established that in all the investigated systems the solubility product of the precipitate varies over wide limits.

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INTRODUCTION OF ACTIVATORS INTO ZnS-LUMINOPHORS BY DIFFUSION

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In earlier papers [1, 1a] it was shown that interesting results can be obtained if the activator is given the opportunity of incorporation into finished ZnS crystals by diffusion at 300-500°. By means of this method, already proposed by Tiede and Weiss [2], it was possible to discover a number of new facts and to approach the study of the crystal chemistry of ZnS luminophors from a fresh angle. In recent years this method has been applied in individual cases by a whole series of authors [3].

The essential fact, in our opinion, is the migration of activators from the crystal. We first described such phenomena as far back as 1941 [1]: silver was displaced from a ZnS crystal by the introduced copper and migrated to the surface of the crystal. Below we shall see that migration phenomena are fairly common and that many of the observed features of ZnS luminophors become intelligible when these phenomena are taken into consideration.

I. It was previously [4] established that the former state of the ZnS crystal into which the activator migrates is decisive both in respect to the amount of activator that can be taken up by the crystal in the luminescent state and in respect to the character of the resultant luminescent centers.

The copper which migrates into an activator-free ZnS crystal possessing a weak blue (azure) luminescence can be incorporated in two different states, one of which gives a darker blue luminescence and the other a green luminescence [1a, 8]. We have studied the distribution of copper between the darker blue and the green state in dependence on its amount, on the duration of calcination which promotes incorporation, and on the temperature.

When a small amount of copper is introduced (10^{-5} g per 1 g ZnS) it is taken up completely in the form of green centers. When larger amounts are introduced (10^{-4} g) it forms predominantly dark-blue centers. Only by very lengthy calcination at very much higher temperatures is it possible to ensure that this large amount of copper (10^{-4} g) is also incorporated in the form of centers of green luminescence [1a].

Reasons have already been given [4] for formation of green centers with small amounts of copper and of dark-blue centers with larger amounts of copper. The weakly luminescent activator-free zinc sulfide prepared at 1250° contains few acceptors and can therefore take up only relatively little copper in the form of centers of green luminescence; incorporation of larger amounts of copper leads to formation of centers of dark-blue luminescence*.

II. If incorporation is carried out for a long period and at high temperatures (1000-1200°), then it is possible to bring even larger amounts of copper (10^{-4} g) into the "green" state [1a]. This is evidently because at such high temperatures and with such prolonged calcination, new, supplementary [Zn] [ ] centers (acceptors) are formed which are immediately occupied by atoms of copper in place of zinc, so that redistribution of the copper takes place: new "green" [Cu] [ ] centers are formed, while the "dark-blue" (Cu) [Cu] [ ] centers lose one atom of Cu and also become "green" Probably the formation of new [Zn] [ ] centers is considerably promoted by the presence of traces of chloride flux which remain in the original luminophors even after most thorough washing [5]. It is known that chlorides exercise a strong desulfurizing action in presence of oxygen [5]. There is reason to believe that these [Zn] [ ] centers, additionally formed at high temperatures, are themselves unstable; if the zinc in them is not immediately replaced by an atom of copper, i.e., if they are not fixed in the form of [Cu] [ ] centers, then they apparently again disappear. In any event, it is not possible to incorporate 10^{-4} g copper per 1 g ZnS in the "green" state if the zinc sulfide is calcined for a long period at

* Bundel and Rusanova [6] reported that at 300° they observed only the incorporation of silver into zinc sulfide (dark-blue luminescence!), and that they were only able to observe the incorporation of copper at higher temperatures (apparently both activators were present simultaneously). It must be pointed out, however, that they used a zinc sulfide treated with sulfur vapor, which contains remarkably few [Zn] [ ] centers, and the incorporation of copper into such a product leads to the development of only a dark-blue luminescence (unless an exceptionally small, specially proportioned amount of copper is used). Since at that time the occurrence of a purely blue luminescence of copper was still unknown in practice, Bundel and Rusanova attributed the blue luminescence of copper to silver. This presumably accounts for their erroneous conclusion that diffusion of copper takes place only at temperatures considerably higher than 300-350°.

high temperature (without flux) prior to admixture of the copper. Apart from that, such a calcination does not result in an intensification of the light-blue luminescence of zinc sulfide; this is evidence against the formation of fresh [Zn] [ ] centers.

III. If 10^{-4} g copper per 1 g ZnS is admixed with activator-free zinc sulfide prepared at 1250°, and if incorporation is effected by diffusion at 450° for 3 hours, then it is found that not all of the admixed copper becomes incorporated in the crystals [1a]. A part of the copper remains (in the form of Cu_2S) on the surface of the grains of zinc sulfide and imparts a grey color to it*. This surface Cu_2S can be removed with KCN solution. After treatment with KCN solution the zinc sulfide again becomes perfectly white and copper can be detected in the solution. If the KCN-treated zinc sulfide is again calcined, then further incorporation of copper into the crystals no longer takes place, but redistribution can occur of the copper already present in the crystals between its two states - "blue" and "green". On recalcination of the preparation not containing copper at the surface of the grains, more copper undergoes incorporation into the ZnS crystals. If, before the recalcination, all that copper had been removed which had not become incorporated during the first calcination, then preparations are finally obtained with a green luminescence, i.e., all the copper entering the crystals passes into the state of green fluorescence [1a]. In the event of non-removal with KCN of the non-incorporated copper at the surface of the grains, the luminescence remained blue after the second calcination since the introduction of supplementary amounts of copper guaranteed the formation of fresh centers of blue luminescence.

IV. As recalled above, there are grounds for believing that the concentration of [Zn] [ ] centers serving as acceptors for the activator is dependent upon the tempe ature to the extent that at 700-1000° it rises and at above 1000° it again falls (this is evidently the consequence of vaporization of zinc from the [Zn] [ ] centers and perhaps also due to another process leading to destruction of these centers-acceptors). At sufficiently low temperatures (300-500°) the concentration of centers-acceptors is also low. In any event we can conclude that at any given temperature there is a certain equilibrium concentration of [Zn] [ ] centers (this concentration also depends upon the presence of certain chemical reagents such as HCl). In other words, a crystal in which a certain concentration of [Zn] [ ] centers was formed at a certain high temperature is a thermodynamically unstable system at another temperature. If, for example, "annealing" is effected at 300-500° (in the absence of desulfurizing agents) of a given ZnS preparation obtained at higher temperatures, then the concentration of [Zn] [ ] centers is bound to exhibit a falling trend. If the original preparation contained copper which replaced zinc in the centers-acceptors, this leads to a certain stabilization of the S-defects (due to the lower volatility of copper or due to copper being more electropositive than zinc). A further consequence is that relatively more copper can be incorporated in the luminescent state into zinc sulfide at high temperature. Nevertheless, at lower temperatures (300-500°) preparations containing much copper in the luminescent state should by no means be thermodynamically stable.

Previous experiments [1a] show that at 300-500° some ZnSCu luminophors prepared at 1050° are actually "supersaturated" with copper. If these preparations are "annealed" at 450°, a portion of the Cu centers of green luminescence disappears; the copper from them in part migrates to the surface of the crystals, and in part combines with the still remaining Cu-centers of green fluorescence, transforming them into Cu-centers of blue luminescence.

Two questions arise out of what has been said. First, why the Cu-centers of green fluorescence are less stable at 300-500°; second, what happens to the Cu-center if it loses an atom of copper. The instability is explained by the fact that the [Cu] [ ] center is an adventitious formation in the lattice, while at not very high temperatures the possible maximum concentration of centers (the "solubility") must be a limiting value. It is not clear, however, what remains in place of the Cu center after loss of a copper atom. An empty site, deficient in both anion and cation, is improbable, since, on the one hand, "over-filling" of the centers with copper is impossible (this would imply formation of centers of blue luminescence), while on the other hand, completely empty sites would remain. The filling of the S-defects with sulfur is also inconceivable, for in our experiments a sulfurizing reagent was lacking; complete "closing" of the hole deficient in anion and cation due to rearrangement of the atoms in the lattice is also highly improbable at such high temperatures.

The following is the most probable explanation (in the light of existing knowledge).

In the past [4] we have repeatedly mentioned that the excess of zinc in the ZnS crystals after calcination in vacuum or in a chlorinating atmosphere (HCl or a chloride flux in presence of oxygen) can be fairly high, and that it becomes accessible to direct visual observation. This excess can only be removed from the crystal with difficulty (i.e., only by calcination at the highest temperatures). It therefore appears probable that in the normal preparation of ZnS luminiophors not only are [Zn] [ ] centers formed but also atoms of zinc in the interstices. Sterically it is not difficult to imagine the penetration of Zn atoms into the interstices; such an incorporation is entirely possible, since otherwise it

* This occurs, of course, only when using a "large" amount of copper (10^{-4} g).

would be impossible to account for the ease with which extraneous atoms diffuse into the ZnS crystal at temperatures not exceeding 300-400° [1]. We can now understand why a copper atom can leave a [Cu] [ ] center during "annealing" of a crystal and what happens to the center after departure of the copper atom: the copper is displaced from the center by zinc present in excess in interstitial positions, the [Cu] [ ] center becoming transformed into a non-luminescent [Zn] [ ] center. With copper and zinc competing in this way for positions in the centers, the end result depends upon the amounts of zinc and copper present: in all experiments on immigration, an excess of copper is formed by distribution over the surface of the crystal of copper salt; due to this excess the copper displaces part of the zinc from the [Zn] [ ] centers so the [Cu] [ ] centers with green luminescence are formed. On carrying out an experiment on emigration of activator, however, we arrive at equilibrium between [Cu] [ ] centers and [Zn] [ ] centers from another, opposed direction; in this case at the start (at high temperatures) the centers become saturated with copper, and copper is entirely absent from the surface of the crystals; consequently the whole displacement caused by the competition between copper and zinc can here lead only to emigration of copper, i.e., to a more or less considerable displacement of copper from [Cu] [ ] centers by zinc.

This hypothesis is supported by the following fact. We established that the emigration of copper from ZnSCu does not occur at all if the ZnSCu luminophor, prior to "annealing", is subjected to prolonged (say 10 hours) calcination at high temperature (above 1000°). "Annealing" (i.e., holding at 450°) of such a ZnSCu luminophor does not result either in emigration of copper to the surface of the crystal or in the development of intensified blue emission. As already recalled, prolonged high-temperature calcination (above 1000°) with a flux leads to marked changes in the ZnCu luminophor: new [Cu] [ ] centers with green luminescence are developed, and at the same time the (Cu) [Cu] [ ] centers with a blue luminescence disappear. We have already said that this indicates the appearance of fresh [Zn] [ ] centers-acceptors capable of giving new Cu centers with a green luminescence. In the light of these facts we can understand the phenomena taking place during prolonged high-temperature calcination of the luminphor without a flux. What is still not clear is why the Cu centers are also stabilized during such a calcination, i.e., why the luminophor does not subsequently exhibit more emigration of copper during "annealing" (300-500°). A possible explanation is that, on the basis of our hypothesis, the copper which leaves the center is replaced by zinc from interstitial positions. If zinc present in the interstitial sites is previously removed by sufficiently prolonged calcination at a sufficiently high temperature, then the crystal no longer contains anything that could replace the copper in the [Cu] [ ] centers, since emigration of zinc is no longer possible.

V. Up to now reference has been made to the incorporation of copper in crystals of ZnS obtained at 1250°. An entirely different picture is obtained if copper is introduced into crystals of ZnS prepared at lower tempeatures, say at 700° [1a]. ZnS luminophors prepared at 700° in general never develop a blue band of luminescence when copper is incorporated. The blue band of copper is inherent only in crystals prepared at high temperature (above 1000°). A decisive part is played by the temperature of formation of the crystals themselves, and not by the temperature of incorporation.

VI. We have previously noted [4,5] that there is a marked difference between oxide-free ZnSCu luminophors, which are characterized in particular by good excitability by α-rays, and ZnSCu luminophors which develop especially prolonged phosphorescence and contain much oxygen. These two types of luminophors also exhibit very marked differences in respect of immigration and emigration of activator. In the first type emigration of copper during "annealing" is observed to a very marked degree: much copper appears on the surface of the grains and correspondingly the preparation luminesces strongly, while the luminescence spectrum undergoes a marked change. The blue copper band becomes so strong and the green band so weak that the luminescence of preparations "annealed" at 450° appears completely blue; nearly the whole of the copper remaining in the ZnS crystals is in the form of (Cu) [Cu] [ ] centers with blue luminescence. Oxygen-containing ZnSCu luminophors with exceptionally prolonged phosphorescence behave quite differently: extremely little copper emigrates to the surface of the grains and the intensification of the blue region of the spectrum is slight.

An equally marked difference between these two types of ZnSCu luminophors is manifested during immigration (incorporation) of added copper. On introducing 10^{-4} g copper per 1 g ZnS at 450° into oxide-free ZnSCu luminophore (with high excitability by α-rays), the luminescence, previously pure-green, becomes purely blue. Nearly all the Cu centers are transformed into (Cu) [Cu] [ ] centers (Fig. 1). But if the same amount of copper is incorporated into a ZnSCu luminophore containing oxygen and possessing exceptionally prolonged phosphorescence, many of the green-fluorescing Cu centers persist (as we see from Fig. 1). For all the highly calcined ZnSCu luminophors accessible to us, we established the same parallelism between excitability by α-rays and extent of emigration of copper during "annealing" and the extent of development of the blue band on incorporation of additional copper*.

* In connection with the physical properties of ZnSCu luminophors free from oxygen, a point still requiring clarification is the maximum possible luminescence yield on excitation with α-rays. Over 20 years ago one of us [9] carried out

On the basis of the foregoing considerations, we may formulate the following general rule relating to emigration of the activator in ZnSCu luminophors; if the addition of a supplementary amount of copper to a ZnSCu luminophor leads to marked intensification of the blue luminescence band of copper, then that luminophor will exhibit also sharply marked effects of emigration of copper when held in the region of 300-500°, the copper emerging on the surface and the blue luminescence band of copper being developed. But if the introduction of copper into a given ZnSCu luminophor is not accompanied by considerable intensification of the blue band, then the effects of emigration of copper are likewise not manifested. (This rule also covers ZnSCu luminophors prepared at low temperatures).

The results submitted on immigration and emigration show that these effects are governed by the interaction of the following three factors: 1) The concentration of [Zn] [ ] centers (acceptors); 2) the amount of copper present at the surface of the crystal; 3) the concentration of zinc in the interstices. The higher the concentration of [Zn] [ ] centers-acceptors, the larger the amount of copper that can be introduced in the luminescent state. When there is a deficiency of these centers, copper in part "condenses" them with formation of (Cu) [Cu] [ ] centers of blue luminescence, while the remaining part of the copper is usually not incorporated in the crystal *. The zinc in the interstices competes with the copper for sites in the acceptors.

VIII. We shall now consider the results obtained in an attempt to increase the concentration of [Zn] [ ] centers (acceptors) by the action of chemical reagents. Emphasis was previously placed upon the special effectiveness of chlorinating agents for desulfurization of zinc sulfide [4,5]. It was also established that the desulfurizing action is manifested even at relatively low temperatures (600-700°), so that it appeared possible to achieve a certain desulfurizing effect with chlorinating reagents also at the temperatures at which the experiments on immigration and emigration of activators were undertaken (300-500°).

Experiments for this purpose revealed an unexpectedly strong action of these reagents at the temperatures indicated. On mixing a little $ZnCl_2$ with the luminophor and heating at 450° (for 1 hour), only a green luminescence is developed under any desired conditions (Fig. 2); in this connection it was immaterial whether the luminophor had previously had a blue luminescence due to supersaturation with copper or whether the copper had been mixed (before heating at 450°) with a luminophor with a green luminescence. In all cases we obtained green-luminescing preparations. The phenomena of emigration, i.e., the separation of Cu_2S at the surface of crystals and the intensification of the blue band were not manifested at all if "annealing" (holding at 300-500°) was effected in presence of $ZnCl_2$. The above-mentioned activator-free zinc sulfide with a very weak light-blue luminescence, prepared at 1250°, likewise did not give a blue luminescence after incorporation of copper if $ZnCl_2$ was present; in this case again, only a green emission was developed**.

The same effect, although less intense, is obtained on mixing in NH_4Cl. The observations of Kroeger and co-work-

extremely thorough determinations of this yield (allowing for absorption of light in the luminophor itself), and calculated an energy yield of 80 % for particularly efficient samples of ZnSCu luminophors. Later Klasens [10] drew attention to two possible errors in such calculations. One of these observations of Klasens has been confirmed, and this correction results in an energy yield lower by a factor of 2, i.e., 40%. This value of the yield is close to that recently found by Broser and Kellman [10] and by Hanle and Rau [12], who obtained a yield of the order of 30%. Thus the question of the order of the maximum energy yield of luminescence during excitation by α-rays has been clarified: in the best luminophor a yield of 30-40% is obtained. As Kellman correctly points out, this magnitude is actually close to the theoretically possible limit: if we remember that the primary act of excitation by α-rays occurs almost exclusively in the ground lattice, i.e., the excitation consists primarily in rapid transfer of electrons from the "occupied" zone to the "conductivity" zone, while the act of radiation corresponds to a two times lower emission of energy in electron-volts, the energy yield cannot be greater than approximately 50%. Thus we have confirmation of the statement that the energy of α-rays is utilized almost completely for excitation of the luminophor.

One should not fall into the error of some authors who believed that the determination of maximum luminescent yield during excitation with α-rays is applicable to any of the usual ZnSCu luminophores prepared for one purpose or another. The determinations of the yield mentioned here were performed on specially active specimens, specially selected from hundreds of specimens of ZnSCu luminophores. The specimens were taken from large technical batches prepared for radioactive luminescent compositions. The excitability with α-rays of the various specimens was by no means uniform [7], and the differences could in part be attributed to certain deliberate or fortuitous variations in the technological conditions, although in part they defied explanation. The object of our determination of the yield was indeed to utilize such a "record" luminophore. The observed chemical differences and characteristics of various ZnSCu luminophores illustrate how large is the number of factors influencing the properties of the final luminophore.

* Part of the excess copper is possibly distributed throughout the interstices. ** This case is represented in Fig. 2.

ers [15] must also be considered to relate to the same type of action of chlorinating agents. These workers exposed finished ZnSCu luminophors to the action of HCl vapor at 450° and thereby obtained an intensification of the green band at the expense of the blue.

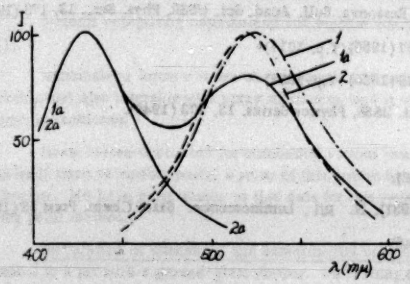

Fig. 1. Spectra of ZnSCu luminophors.

1) Content of ZnO with exceptionally prolonged phosphorescence; 1a) the same after incorporation at 450° of additional copper (10^{-4} g Cu per 1 g ZnS); 2) without ZnO (with high excitability by α-rays); 2a) the same after incorporation at 450° of additional copper (10^{-4} g Cu per 1 g ZnS).

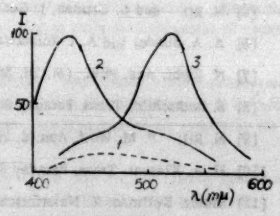

Fig. 2. Spectra of ZnS luminophors.

1) Activator-free, prepared at 1250°; 2 the same after incorporation of copper (10^{-4} g per 1 g ZnS) at 450°; 3) the same after incorporation of the same amount of copper at 450° in presence of $ZnCl_2$.

Thus the desulfurizing action of chlorinating agents takes place even at temperaturesof several hundred degrees; it also leads here to the formation of new [Zn] [ ] centers (acceptors) so that the number of "green" [Cu] [ ] centers is increased, while the number of "blue" (Cu) [Cu] [ ] centers falls. Concerning the mechanism of desulfurization at such low temperatures, we must assume that one atom of sulfur is at first moved to the surface of the crystal, and then this defect is transferred to the interior of the crystal (alternating skipping of S^{--} ions from place to place). Such transfers of defects do not constitute anything unusual in crystal chemistry.

In connection with the fact that at the present time two different states of copper in zinc sulfide are known, we may recall that according to our earlier observations [1] iron can also exist in two forms in zinc sulfide; in one form it acts as an inhibitor, and in the other form it is inactive. At that time we showed experimentally that cobalt and nickel are also incorporated into zinc sulfide in two different states, one of which again quenches the visible luminescence of other activators, while the other does not quench it *. In the first of these states these three elements give red and infra-red emission, and thereby confirm the observation [14] that quenchers of the type of Fe, Co and Ni do not simply convert the whole of the energy taken up by them into heat energy, as was previously assumed, but emit it in the form of red and infra-red luminescence.

The crystal-chemical character of these two states of iron, cobalt and nickel is not considered in the present paper.

SUMMARY

1. The phenomena of diffusion of an activator (copper) into ZnS crystals and the emigration of the activator from the crystals are investigated. The results obtained can be used for verifying models of previously proposed luminescence centers.

2. The possibility is studied of development of sulfur defects inside the crystals by the action of desulfurizing agents at the surface of the finished crystal. It is shown that at 400-500° such an effect occurs, but that the defects developed in this manner are not permanent unless an atom of zinc, which had been deprived of sulfur, is replaced by an atom of a more electropositive metal, for example by an atom of copper.

* It is possible that these elements also exercise a quenching action in the second state but a very much weaker one.

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* T.p. = C.B. Translation pagination

MELTING POINT DIAGRAM OF THE SYSTEM HEXACHLORAN-NAPHTHALENE

N. P. Gavrish

Systems comprising naphthalene and organic compounds have been investigated by V. M. Kravchenko and others [1].

Naphthalene forms a series of compounds with organic and inorganic substances. Hexachloran (hexachlorocyclohexane) also interacts with many substances, and it was therefore interesting to study the interaction of naphthalene with hexachloran.

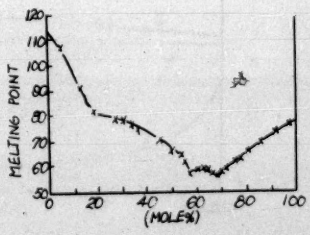
Hexachloran is utilized for combating various pests of agricultural plants. Naphthalene readily evaporates and is itself toxic to various pests; a study of this system by various methods of physical chemical analysis is therefore of interest. We have been unable to find data for this system in the literature. We investigated the system by the melting point method.

Preparation of substances and experimental procedure. Hexachloran, chem. pure, with a faint-greyish color was stored in a jar with a ground-glass stopper. On melting it changes into a colored and transparent liquid. M. p. 112.5°. Hexachloran exists in several modifications with different melting points. The preparation that we used corresponds in melting point to γ-hexachloran.

Naphthalene, chem. pure grade, was distilled and then twice sublimed and dried. The preparation was stored in a bottle with a ground-glass stopper. The purified preparation of naphthalene had m.p. 80.1°.

Thermal analysis. Freezing point measurements were performed with a standard thermometer in the special vessel described by Ya. A. Fialkov and A. A. Kuzmenko [2]. The melt was prepared in the vessel with the ground glass stopper itself, thus precluding access of moisture to the substances under investigation. Results of measurements are detailed in the table and plotted in the diagram.

Content of hexachloran (in mole %)	Melting point	Content of hexachloran (in mole %)	Melting point
100	112.50	39.5	57.75
96.6	107.00	37.3	58.00
87.2	90.50	35.1	58.25
82.2	81.00	33.4	57.00
72.5	79.50	31.7	56.5
68.9	78.75	30.5	57.75
66.2	77.00	28.1	59.25
63.4	74.50	24.7	62.50
55.1	70.00	22.8	63.25
49.7	66.50	20.0	65.50
46.7	65.50	14.4	70.00
44.0	62.00	8.03	74.25
42.3	57.00	2.2	77.25
		0	80.1



Melting point diagram of the system hexachloran-naphthalene

The melt darkens on melting and becomes light-grey on cooling. In some cases, notwithstanding intensive stirring and slow cooling, supercooling was observed to the extent of 2-4°.

The melting point diagram has a pronounced maximum corresponding to the compound $2C_{10}H_8 \cdot C_6H_6Cl_6$ with m.p. 58.25°.

The maximum of the melting point diagram is flat; this indicates that the compound formed is relatively unstable [3].

SUMMARY

By the method of thermal analysis the formation was established in the system hexachloran-naphthalene of a compound $2C_{10}H_8 \cdot C_6H_6Cl_6$, melting at 58.25°. The maximum on the melting point diagram is flat; this indicates that the compound formed is relatively unstable.

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Ukrainian Academy of Agriculture

TRANSFORMATIONS OF HYDROCARBONS IN PRESENCE OF OXIDE CATALYSTS

VII. AROMATIZATION OF BINARY ALKANE-AROMATIC HYDROCARBON MIXTURES OVER CHROMIUM CATALYST

Yu. N. Usov and N. V. Sidorova

Relatively little study has been devoted to the question of the influence of aromatic hydrocarbons upon the course of the catalytic aromatization of paraffinic hydrocarbons. The literature contains only a few papers on the catalytic aromatization of mixtures of aliphatic and aromatic hydrocarbons.

Oblad, Marschner and Heard [1] investigated the influence of additions of toluene upon the aromatization of n-heptane over a chromium catalyst. Green [2] studied the influence of toluene on the yield of aromatic hydrocarbons during cyclization of mixtures of n-heptane with toluene over a molybdenum catalyst.

Plate and Tarasova [3] investigated the behavior of heptane-toluene and heptene-toluene mixtures in presence of vanadium catalyst and reached a whole series of interesting conclusions about the dependence of toluene yields on the composition of the starting mixture.

In the present investigation we studied the effect of aromatic hydrocarbons in presence of a chromium catalyst.

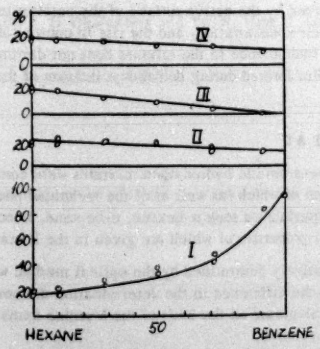

Fig. 1. Aromatization of hexane-benzene mixtures.

I) Yield of benzene reckoned on original hexane; II) amount of freshly formed benzene; III) amount of olefins in catalyzate; IV) amount of olefins reckoned on original hexane.

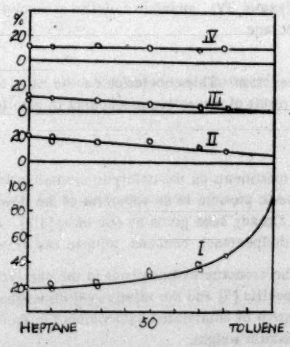

Fig. 2. Aromatization of heptane-toluene mixtures.

I) Yield of toluene reckoned on the original heptane; II) amount of freshly formed toluene; III) amount of olefins in catalyzate; IV) amount of olefins reckoned on original heptane.

The aromatization of hexane-benzene, heptane-toluene and isooctane-o-xylene mixtures was studied with reference to five mixtures of varying composition.

In addition a study was made of the behavior of pure n-hexane, n-heptane, isooctane, benzene, toluene and o-xy-

lene over the same catalyst. The composition of the starting mixtures and the experimental results are shown graphically in Figs. 1, 2 and 3. Inspection of the graphs indicates that for all the three mixtures studied, the yield of aromatic hydrocarbon (calculated on the basis of the paraffinic hydrocarbon in the mixture) increases with decreasing content of the paraffin in the original mixture (curve I); but the amount of freshly formed aromatic hydrocarbon decreases with decreasing content of paraffin in the mixture (curve II). The general course of the curves representing the yield of aromatic hydrocarbons in relation to the original paraffin indicates that the extent of transformation of the paraffinic hydrocarbons increases with falling content of the latter in the original mixture. A possible explanation of this is that the paraffinic hydrocarbons are adsorbed at the surface of the chromium catalyst more readily than aromatics.

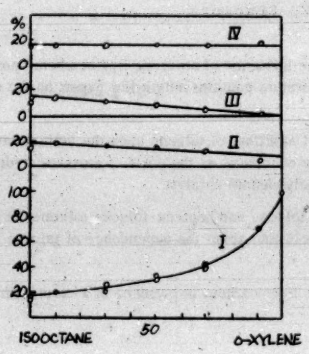

Fig. 3. Aromatization of isooctane-o-xylene mixtures.

I) Yield of xylene reckoned on original isooctane; II) amount of freshly formed xylene; III) amount of olefins in catalyzate; IV) amount of olefins reckoned on original isooctane.

In the case of aromatization of hexane-benzene mixtures, curves III and IV (Fig. 1) show that the amount of unsaturated hydrocarbons in the catalyzate and their yield, reckoned on the starting hexane, decrease with decreasing amount of hexane in the mixture.

This relationship arises evidently because an increase in the amount of benzene in the mixture hinders adsorption of hexane molecules on that part of the active surface of the catalyst on which the paraffin is dehydrogentated to olefin, so that the yield of olefins, reckoned on the original hexane, decreases.

In the case of aromatization of heptane-toluene and isooctane-o-xylene mixtures, curves III and IV (Figs. 2 and 3) show that the amount of unsaturated hydrocarbons formed is directly proportional to the amount of parrafin in the mixture, while their yield (reckoned on the paraffin hydrocarbon contained in the starting mixture) remains constant. Thus, heptane and isooctane, when dehydrogenated to olefins, are adsorbed by the active surface of the catalyst in proportion to their concentration, and the rise in content of the aromatic hydrocarbon in the mixture does not diminish the role of this reaction. This conclusion can be valid only when the olefins formed during dehydrocyclization of the paraffins are the result of a reaction proceeding in parallel [10].

EXPERIMENTAL

Experiments on the catalytic aromatization of binary alkane-aromatic hydrocarbon mixtures were conducted at atmospheric pressure in an apparatus of the flow type, a description of which (as well as of the technique and the catalyst) has already been given by one of us [4,5]. As starting raw materials we took n-hexane, n-heptane, isooctane (2,2,4-trimethylpentane), benzene, toluene and o-xylene, the physical properties of which are given in the literature [6].

The aromatic hydrocarbons in the catalyzates were quantitatively determined by the optical method with the aid of the specific [7] and the relative [8] dispersion. In all cases the difference in the determination did not exceed 1%. The content of unsaturated hydrocarbons in the catalyzates was calculated on the basis of the bromine number [9] and the molecular weight.

Experiments with heptane-toluene mixtures were carried out under "standard" conditions at 475° and a space velocity of feed of the starting material into the reactor of 0.5; for mixtures of hexane and benzene the temperature was 490° and for mixtures of isooctane and o-xylene it was 500° with space velocity as before.

This choice of experimental conditions ensured that the degree of transformation of the pure alkanes and of their mixtures with aromatic hydrocarbons was such that secondary reactions and cracking only represented a small fraction of the main direction of the process – the dehydrocyclization reaction. The content of aromatic hydrocarbons in the original mixtures varied between 10 and 90%.

SUMMARY

1. A study was made of the aromatization of hexane-benzene mixtures at 490°, of heptane-toluene mixtures at 475°, and of isooctane-o-xylene mixtures at 500° over chromium catalyst at feed velocity of starting material of 0.5 vol./vol. catalyst/hour.

2. It was shown that the amount of freshly formed aromatic hydrocarbons falls with decreasing content of paraffinic hydrocarbons in the starting mixture.

3. It was established that the yield of aromatic hydrocarbons, reckoned on the original paraffinic hydrocarbon, increases with decreasing content of the latter in the original mixture.

4. It was found that for mixtures of heptane with toluene and of isooctane with o-xylene the amount of unsaturated hydrocarbons formed is proportional to the content of paraffin in the original mixture, while their yield, reckoned on the original paraffin, remains constant. For hexane-benzene mixtures the amount of unsaturated hydrocarbons formed and their yield (calculated on the original hexane) decrease with decreasing content of hexane in the original mixture.

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ADDITION OF HYDROGEN TO AN ISOLATED DOUBLE BOND UNDER THE ACTION OF CALCIUM AMMINE

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It is usually assumed that the isolated double bond in aliphatic and alicyclic hydrocarbons is reduced only by catalytically activated hydrogen and is not reduced by the so-called nascent hydrogen. In 1951 we were able to show for the first time that such a-reduction is possible; for example under the action of calcium ammine, which breaks down according to the equation $Ca(NH_3)_6 \rightarrow Ca(NH_2)_2 + 4NH_3 + H_2$, 2,5-dimethylhexene-2 is partly reduced to 2,5-dimethylhexane [1]. Recently Greenfield, Friedel and Orchin [2] observed that 1-hexene is partly reduced by sodium in liquid ammonia solution in presence of methyl alcohol. 2-Hexene is not reduced under these conditions; nor does a solution of sodium in liquid ammonia reduce 1-hexene in the absence of the alcohol. On the basis of these experiments we may conclude that α-monoolefins are susceptible to reduction not solely by catalytically activated hydrogen.

The extremely out-of-date but still frequently employed term "nascent hydrogen" is usually used in connection with substances capable of bringing about the addition of hydrogen to unsaturated compounds; the substances may or may not evolve free hydrogen during the reaction. Examples are hydrofluoric acid [3], which dissociates under heating according to the equation $2HI \rightleftharpoons H_2 + I_2$, amalgams of a number of metals in presence of water or of aqueous solutions of acids [4-6], metals + acid [7], alkali metals + alcohol [8], alkali and alkaline earth metals in liquid ammonia solution [9-12], alkali metals in liquid ammonia with addition of alcohol or water [12-14], and calcium ammine [15-21].

There is no doubt that the mechanism of the reducing action of all these systems can vary, for "nascent hydrogen" as such does not by any means always play a decisive part. Kekulé [4] assumed the following reactions to account for the reducing action of sodium amalgam:

$$2Na\,(amalgam) + 2H_2O \rightarrow 2NaOH + 2H$$
$$>C{=}C< + 2H \rightarrow >CH{-}CH<$$

Willstätter, however, showed in 1928 (22) that the pure amalgam, acting quickly and with high utilization of hydrogen, does not evolve it in the free state on reaction with water. For this reason he put forward the hypothesis that on reduction of a number of aromatic compounds with sodium amalgam the first step is addition of sodium at the double bond, and this is followed by replacement of the sodium by the hydrogen of the water:

$$>C{=}C< + 2Na\,(amalgam) \rightarrow >CNa{-}NaC<$$
$$>CNa{-}NaC< + 2H_2O \rightarrow >CH{-}CH< + 2NaOH$$

According to Wooster [13] the vigorous evolution of hydrogen during reduction of toluene with sodium in liquid ammonia, catalyzed by the addition of an iron salt to the reaction mixture, likewise does not promote the addition of hydrogen to toluene.

Willstätter's hypothesis was supported by the observations of Schlenk and Bergmann [8] who succeeded in preparing, in an ether medium, a series of sodium derivatives of phenyl-substituted ethylenes, fulvenes and aromatic hydrocarbons of condensed structure; by the action of water or alcohols these derivatives were easily converted into the corresponding dihydro products. At about the same time Ziegler [23], Wooster and Ryan [24] and Gilman and Railie [25] by the action of sodium, lithium, calcium, strontium and barium in a medium of liquid ammonia on various phenyl-substituted ethylenes obtained, in addition to products of reduction and polymerization of these hydrocarbons, products of addition of the above metals to the olefinic double bond; in these compounds the metal could be replaced by hydrogen under the action, for example, of ammonium salts. All these facts would appear to confirm the scheme proposed by Willstätter, but only when applied to a comparatively limited range of substances, in particular to those compounds in which the double bond was conjugated with an aromatic ring. Benzene and its simplest homologs do not give addition products with sodium, and up to now not a single case is known of reduction of these hydrocarbons with sodium amalgam or with a solution of sodium in liquid ammonia.

In 1916, however, Dumansky and Zvereva [15], showed that benzene is reduced to di- or tetrahydro derivatives with calcium ammine which decomposes (as indicated above) with release of hydrogen; Kazansky and co-workers [16-18,

21] later studied this reaction in detail not only for benzene and its homologs but also for diene hydrocarbons, which form monoolefins admixed with paraffins. Wooster [13,26] observed that benzene hydrocarbons can be reduced by a solution of sodium in liquid ammonia on addition of water or alcohol.

These observations would appear to be indicative of the special role of free nascent hydrogen; also in these cases, however, it is more correct to assume another reduction mechanism. While studying the properties of solutions of the alkali and alkaline earth metals in liquid ammonia and the reactions taking place in them, Kraus [27-31] arrived at the conclusion that these reactions are ionic in character. He suggested that sodium, on dissolving in liquid ammonia, in part forms the positive Na^+ ion; the negative ions are free electrons solvated by molecules of ammonia. According to Kraus the process of reduction of the double bond goes in two steps; the first step is the formation of a divalent hydrocarbon anion due to addition to the double bond of two electrons: $>C{=}C< + 2\bar{e} \rightarrow >\bar{C}{-}\bar{C}<$; the second step is addition to this anion of two of the protons present in liquid ammonia and formed as a result of dissociation of the latter: $NH_3 \rightleftharpoons NH_2^- + H^+$. The product of reduction, containing the grouping $>\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}<$, is a very weak acid in liquid ammonia solution, considerably weaker than ammonia itself; this accounts for the possibility of its formation under the specified conditions.

In 1947 Birch [12] submitted a series of facts in support of such a reduction scheme for a compound of the type of

and others, while Greenlee and Fernelius [32] used it to explain the formation of trans-alkenes during reduction of acetylenic hydrocarbons by sodium in liquid ammonia solution. In their opinion the trans-isomers are formed because of the tendency of the added electrons to occupy positions most distant from one another, and this determines the subsequent trans-addition of protons:

$$RC{\equiv}CR + 2\bar{e} \rightarrow \underset{\bar{e}}{\overset{\bar{e}}{RC{=}CR}} + 2H^+ \rightarrow \underset{H}{\overset{H}{RC{=}C}}{-}R.$$

If we accept Kraus's theory, then the increased reducing capacity of a solution of sodium in liquid ammonia after addition of alcohol (observed in reduction of 1-hexene or benzene) must be attributed not to the formation of nascent hydrogen but to the alcohol being a most effective supplier of protons, since the proton affinity of the alcohol anion is less than that of the NH_2^- anion in liquid ammonia, and the alcohol in this medium acquires the properties of an acid. Evolution of hydrogen, however, is a side reaction between protons and electrons and does not influence the reduction.

Evidently calcium ammine is a reducing system just as strong as, or even stronger than, sodium + liquid ammonia + alcohol, since (as already noted) it is capable of reducing both benzene and its homologs and dienes, as well as some monoolefins, and not only α-olefins but also olefins with other structures. Little has hitherto been known about the properties and structure of calcium ammine (and ammines of other alkaline earth metals). It was first studied by Moissan [33] who prepared it at room temperature and proposed the formula $Ca(NH_3)_4$. Later Kraus [27] showed that its composition corresponds to $Ca(NH_3)_6$. Biltz and Hüttig [34] confirmed the conclusions of Kraus and showed that spontaneous breakdown of ammines of the alkaline earth metals goes according to the equation $Ca(NH_3)_6 \rightarrow Ca(NH_2)_2 + 4NH_3 + H_2$. Botolfsen [35] showed, in a study of the decomposition of calcium ammine under various conditions, that decomposition only takes place according to the foregoing equation under the pressure of the freely evolved gas and at low temperatures, whereas at elevated temperature and in vacuum calcium nitride and hydride are also formed. Kraus [30] observed that both the solution of calcium ammine in liquid ammonia and the solid ammine conduct the electric current like metals, and therefore concluded that solid calcium ammine contains, in addition to complex molecules, ions and free electrons:

$$Ca(NH_3)_6 \rightleftharpoons [Ca(NH_3)_6]^{++} + 2\bar{e}.$$

Calcium ammine has not been studied more closely right down to the present time, and current literature [36, 37] quotes the theories of Kraus about its nature.

The spontaneous breakdown of the ammine with release of hydrogen might be explained by the acidic dissociation of the $[Ca(NH_3)_6]^{++}$ ion with release of a proton:

$$[Ca(NH_3)_6]^{++} \rightarrow [Ca(NH_3)_5NH_2]^+ + H^+,$$

and subsequently:

$$[Ca(NH_3)_5NH_2]^+ \rightarrow [Ca(NH_3)_4(NH_2)_2] + H^+;$$

$$[Ca(NH_3)_4(NH_2)_2] \rightarrow Ca(NH_2)_2 + 4NH_3;$$

$$2H^+ + 2\bar{e} \rightarrow 2H \rightarrow H_2.$$

An analogy to such an acidic dissociation of calcium ammine is found, for example, in the dissociation of platinum hexammine described by Brönsted [38] and by Grinberg and Faerman [39]. The latter authors showed that platinum ammines $[Pt(NH_3)_6]Cl_4$, $[Pt(NH_3)_5Cl]Cl_3$, $[Pt(NH_3)_4Cl_2]Cl_2$, etc. can (to be precise, in aqueous solutions) split off protons according to the equation $[Pt(NH_3)_6]^{++++} \rightarrow [Pt(NH_3)_5NH_2]^{+++} + H^+$, with formation of complex amido compounds and are therefore weak acids whose acidity declines with falling number of coordinatively bound NH_3 molecules.

If we accept the ideas developed above, then we can assume that the reduction of aromatic and unsaturated hydrocarbons in presence of calcium ammine likewise proceeds according to the scheme put forward by Kraus and Birch, i.e., it can be regarded as an ionic process comprising two steps: addition of electrons to the double bond and addition of protons to the resultant hydrocarbon anion. In this case again, the hydrogen released in the free state can then be regarded as a by-product which does not directly take part in the reduction reaction.

In the present paper we describe the partial reduction of the following olefins: 2-methylbutene-1, 2-methylbutene-2, 3-methylbutene-1, mixtures of hexene-2 with hexane-3, and mixtures of cyclohexene with 2,5-dimethylhexene-3. All these olefins, apart from 2-methylbutene-2, are partly reduced by repeated reaction with calcium ammine. 2-Methylbutene-2- is not reduced at all even after two reductions. The most far-reaching reduction (20%) occurs with 3-methylbutene-1, the double bond of which is in the α-position.

A small amount of unreacted calcium may remain in the reaction vessel during preparation of calcium ammine, and some calcium hydride might be formed during distillation of the reduction products owing to decomposition of calcium ammine. The question therefore arises whether reduction of the isolated double bond might not be the result of the catalytic action of metallic calcium or calcium hydride.

The following experiments were undertaken to clarify this point. Diisobutenyl (2,5-dimethylhexadiene-1,5) and 2,5-dimethylhexene-2 were passed together with hydrogen through a tube packed with pieces of calcium or calcium hydride at 200° (the maximum temperature at tainable in our experiments during distillation of reduction products from the reaction flask). In no case was a fall observed in the constants of the original hydrocarbons such as might have testified to the appearance in the reaction mixture of hydrocarbons more saturated than the original hydrocarbons.

EXPERIMENTAL

Procedure for reduction and examination of reaction products. The apparatus for carrying out the reactions has already been described [17]. It was improved by attaching a cooled dropping funnel with a ground-glass connection to one of the inlets. The tube of the funnel reached nearly to the bottom of the flask. In the apparatus, cooled to −5 to −10°, was placed a weighed amount of metallic calcium in the form of turnings or dust, and ammonia from a cylinder was passed in through the funnel for 3-4 hours via two drying bottles containing solid potassium hydroxide; the calcium was thereby converted into golden-yellow ammine with a volume several times greater.

The flask was then connected to a coil with a siphon cooled to −40 to −50°, and through the funnel was slowly run the hydrocarbon to be reduced. After 2-4 hours' standing at room temperature, the product of reduction was slowly distilled into the coil by gently heating the flask over a gauze. Two layers condensed in the flask: a lower layer of hydrocarbons and an upper ammoniacal layer. The lower layer was separated with the help of the siphon, washed with water, dried over calcium chloride, and distilled over metallic sodium from a Favorsky flask. It was then examined by determination of refractive index, specific gravity, and Kaufmann bromine number.

Reduction of olefins: a) Isopentenes were obtained by catalytic hydrogenation of isoprene. After further distillation in a column with 40 theoretical plates the hydrocarbons possessed the following constants:

	Boiling point (760 mm)	n_D^{20}	d_4^{20}	Bromine number
3-Methylbutene-1	20.1°	1.3645	0.6285	228.3
2-Methylbutene-1	31.1	1.3782	0.6498	225.7
2-Methylbutene-2	38.5	1.3880	0.6610	227.9

The literature constants of the hydrocarbons are:

	Boiling point	n_D^{20}	d_4^{20}
3-Methylbutene-1	20.06°	1.3643	0.6272
2-Methylbutene-1	31.16	1.3778	0.6504
2-Methylbutene-2	38.53	1.3874	0.6623

For C_5H_{10} ($\bar{F}$) the calculated bromine number was 226.6.

All the hydrocarbons were twice interacted with calcium ammine in the apparatus described above. In all experiments about 3 g-atoms calcium was taken per 1 mole of hydrocarbon. Results of reduction are set forth in Table 1.

TABLE 1

Hydrocarbon	1st reduction					2nd reduction				
	n_D^{20}	d_4^{20}	bromine number	olefins (in %)	paraffins (in %)	n_D^{20}	d_4^{20}	bromine number	olefins (in %)	paraffins (in %)
3-Methylbutene-1	1.3640	–	213.4	94.1	5.9	1.3630	0.6230	181.8	80.0	20.0
2-Methylbutene-1	1.3763	0.6449	210.0	93.7	6.7	1.3771*	0.6454*	199.1	87.8	12.2
2-Methylbutene-2	1.3878	0.6610	227.9	100.4	0	1.3882	0.6608	227.0	100	0

b) Mixture of hexene-2 and hexene-3. The starting material for the reduction was a mixture of approximately equal amounts of hexene-2 and hexene-3 obtained by distillation in a column of 40 theoretical plates of the product of reduction of dipropenyl (2,4-hexadiene) with calcium ammine.

B. p. 65.6-67.2° (752 mm), n_D^{20} 1.3950, d_4^{20} 0.6790. Found bromine number 188.2, calculated for C_6H_{12} ($\bar{F}$) 190.1.

Reduction was carried out twice in succession. For each mole C_6H_{12} was taken about 4 g-atoms calcium.

On reduction the constants of the hydrocarbon mixture and its content of unsaturated and saturated hydrocarbons changed in the following manner:

	n_D^{20}	d_4^{20}	Bromine number	Olefins (in %)	Paraffins (in %)
After 1st reduction	1.3937	0.6782	177.8	93.5	6.5
" 2nd "	1.3922	0.6762	168.8	88.4	11.6

c) 2,5-Dimethylhexene-3 was prepared by distillation in a column of 40 theoretical plates of the product of reduction of diisocrotyl with calcium ammine. The prepared hydrocarbon had the following constants:

B. p. 101.5-102° (760 mm), n_D^{20} 1.4045, d_4^{20} 0.7017. Found bromine number 145.8, calculated for C_8H_{16} ($\bar{F}$) 142.7.

Reduction was carried out twice in succession. For each mole hydrocarbon was taken about 10 g-atoms calcium. The properties and composition of the reduction product changed as follows on reduction:

	n_D^{20}	d_4^{20}	Bromine number	Olefins (in %)	Paraffins (in %)
After 1st reduction	1.4067	0.7065	137.3	96.5	3.5
" 2nd "	1.4065	0.7062	127.3	89.1	10.9

The product of reduction of 2,5-dimethylhexene-3(2,5-dimethylhexane) has a lower specific gravity (0.6936) and refractive index (1.3925), and consequently on reduction of 2,5-dimethylhexene-3 both the specific gravity and refractive index of the resultant mixture should be lower than for the starting mixture, whereas in the present case they were higher and the bromine number of the mixture fell. Partial isomerization of 2,5-dimethylhexene-3- to 2,5-dimethylhexene-2 had evidently occurred (see note to Table 1 for constants of the second compound).

d) Cyclohexene was obtained by dehydration of cyclohexanol. After distillation in a column it had the following constants:

B. p. 82.5° (755 mm), n_D^{20} 1.4470, d_4^{20} 0.8109. Found bromine number 193.3, calculated for C_6H_{10} ($\bar{F}$) 195.1.

* The rise in n_D^{20} and d_4^{20} is probably the result of partial isomerization of 2-methylbutene-1 to 2-methylbutene-2 under the influence of calcium amide formed during the reaction.

Reduction of cyclohexene was carried out three times. In all cases 3.5 g-atom calcium was taken for each g mole of hydrocarbon. The properties of the reduction product and the composition changed as follows:

	n_D^{20}	d_4^{20}	Bromine number	Olefins (in %)	Paraffins (in %)
After 1st reduction	1.4446	0.8055	173.3	88.9	11.1
" 2nd "	1.4430	0.8046	165.5	84.5	15.5
" 3rd "	1.4425	0.8036	161.5	82.8	17.2

Experiments on hydrogenation in presence of metallic calcium and calcium hydride. Technical calcium and calcium hydride (imported) were used. On reaction with water the latter evolved 99.5% of the theoretical amount of hydrogen. The starting diisobutenyl, synthesized from methallyl chloride and magnesium, had the following constants:

B.p. 113.1° (760 mm), n_D^{20} 1.4302, d_4^{20} 0.7412. Literature data [40]: B.p. 114.3°, n_D^{20} 1.4293, d_4^{20} 0.7423.

The starting 2,5-dimethylhexene-2, prepared by reduction of diisobutenyl with calcium ammine, had the following constants:

B.p. 112.6° (760 mm), n_D^{20} 1.4160, d_4^{20} 0.7188, bromine number 145.8. Literature data [41]: B.p. 112-112.2°, n_D^{20} 1.4146, d_4^{20} 0.7202.

Calcium or calcium hydride was placed in a catalytic tube (length of bed 30 cm, diameter of tube 13 mm) through which was passed the hydrocarbon in a hydrogen stream at a temperature of 200°.

Results of the experiments are set forth in Table 2.

TABLE 2

Catalyst	Hydrocarbon	n_D^{20}		Bromine number	
		before experiment	after experiment	before experiment	after experiment
Calcium	Diisobutenyl	1.4302	1.4315	–	–
	2,5-Dimethylhexene-2	1.4160	1.4164	145.8	144.2
Calcium hydride	Diisobutenyl	1.4302	1.4474	–	–
	2,5-Dimethylhexene-2	1.4160	1.4158	145.8	146.2

The slight rise in the refractive index of diisobutenyl when passed over calcium and calcium hydride is evidently due to the facility with which the diene isomerizes at high temperatures.

SUMMARY

1. The possible mechanism of the reducing action of solid calcium ammine was evaluated.

2. Partial reduction was effected with calcium ammine of the following monoolefins: 3-methylbutene-1, 2-methylbutene-1, 2-methylbutene-2, mixture of hexene-2 and hexene-3, and mixture of 2,5-dimethylhexene-3 and cyclohexene. The amounts of paraffinic hydrocarbons formed were determined.

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CONDENSATION OF BENZENE WITH SOME SYMMETRICAL CHLOROETHERS

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The condensation of benzene with symmetrical chloroethers has been relatively little studied. More attention has been given to the condensation of benzene and its homologs with unsymmetrical chloroethers [1], as well as to the reaction of benzene with α,α'-dichloromethyl ether [2]. Using carbon disulfide as solvent at low temperatures, Sommelet [3] showed that the condensation of benzene with unsymmetrical chloroethers in presence of $AlCl_3$ proceeds in two directions, either ethers or aryl-alkyl chlorides being formed.

In view of the available data we were interested in studying the condensation of benzene with symmetrical chloroethers, both α- and β-substituted. The study was commenced by condensing benzene with α,α'-dichloroethyl, β,β'-dichloroethyl, and α,α'-dichloromethyl ethers.

These experiments established that the main reaction products are, respectively, unsymmetrical diphenylethane, dibenzyl and diphenylmethane.

A feature of these syntheses was the use of a large excess of benzene as solvent. A study was made of the influence of temperature and of the amount of $AlCl_3$ upon the composition and yield of end products. The optimum conditions of condensation are detailed in the table.

A number of statements have appeared about the low reactivity of the Cl atoms in β,β'-dichloroethyl ether and about the inertness of the latter in the Gustavson-Friedel-Crafts reaction [4]. As the experiments showed, however, the condensation of benzene with β,β'-dichloroethyl ether proceeds readily in presence of anhydrous $AlCl_3$.

The expected ethers were not found, but they were possibly formed as intermediate products. A special comparative experiment with dibenzyl ether in benzene in presence of $AlCl_3$ showed that in this case diphenylmethane is obtained in high yield.

Condensation of benzene with chloroethers

Chloroethers	Charged			Temperature	Duration (min.)	Main products of reaction	Yield		B.p. at pressure (in mm)	Melting point
	benzene* (in ml)	chloroether (in g)	$AlCl_3$ (in g)				(in g)	(in %)		
α,α'-Dichloroethyl	150	6	10	78°	80	Unsymm. diphenylethane **	7	46	129° (8)	–
β,β'-Dichloroethyl	400	12	50	78°	90	Dibenzyl***	18	60	137(10)	49.5
α,α'-Dichloromethyl	300	10	20	18-20	100	Diphenylmethane ****	23.64	81.5	130(12)	24.6

* Allowing for the benzene taken for dissolving the chloroether.

** d_4^{20} 1.0057, n_D^{20} 1.5815, MR_D 60.2; calculated 59.8. Found %: C 92.8, 92.7; H 7.0, 6.8. Calculated %: C 92.3; H 7.7. Literature data: B.p. 268-270°, 148° (22 mm), 136° (12 mm), d_0^{20} 1.0033, n_D^{20} 1.5761 [6].

*** Literature data [6]: M.p. 52°, B.p. 284°. No depression in mixed melting test.

**** Literature data [6]: M.p. 26-27°, B.p. 261-262°, 158° (35 mm), 120° (10 mm). No depression in mixed melting test.

EXPERIMENTAL

α,α'-Dichloroethyl ether was synthesized from acetaldehyde and hydrogen chloride [5]. The ether had b.p. 114-115°, d_4^{20} 1.1157, n_D^{20} 1.4275. Literature data: b.p. 112.5-114°, d_4^{25} 1.106, n_D^{25} 1.4186 [6].

β,β'-Dichloroethyl ether had b.p. 70-71° (15 mm), d_{20}^{20} 1.221, n_D^{20} 1.458. Literature data: b.p. 70° (15 mm), d_{20}^{20} 1.213, n_D^{20} 1.457 (6).

α,α'-Dichloromethyl ether was prepared by Tishchenko's method [7] and had b.p. 106-108°, n_D^{20} 1.4445. Literature data: b.p. 104-105°, n_D^{21} 1.435 [6].

Alkylation was effected in a pear-shaped four-necked flask of 500 ml capacity, fitted with stirrer, thermometer, reflux condenser and dropping funnel. The same procedure was followed in all experiments.

$AlCl_3$ was suspended with vigorous stirring in benzene, and the chloroether dissolved in benzene was added from the dropping funnel. At the end of the reaction, the mixture was run in small portions into cooled water acidified with hydrochloric acid. The benzene layer was then washed 3-4 times with water and then dried before fractionation. The benzene was taken off at atmospheric pressure and the reaction products were distilled in vacuum. The main reaction products were subsequently purified by fractionation or by recrystallization in all cases; by-products were small amounts of high-boiling non-crystallizing liquids. A small amount of resinified products always remained in the flask after distillation.

SUMMARY

Condensation of benzene with α,α'-dichloroethyl, β,β'-dichloroethyl and α,α'-dichloromethyl ethers, carried out with a large excess of benzene in presence of $AlCl_3$, leads to formation of diphenylalkanes regardless of whether the starting substances contain halogen in the α- or β-position.

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THE REACTION OF PROPYLENE OXIDE WITH ALCOHOLS

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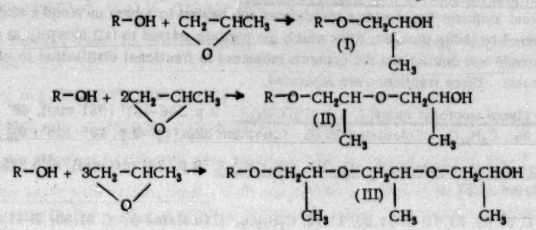
As repeatedly reported in the literature [1-5], the reaction of propylene oxide with alcohols leads to formation of monoethers of propylene glycol. In isolated cases the products of reaction with some lower alcohols have been isolated and identified, and their structure has been accurately established. High-molecular products of condensation of propylene oxide with alcohols find application as solvents for nitrocellulose lacquers, greases, hydraulic fluids, etc.

In the present research we set out to establish the qualitative features of the formation, apart from monoethers of propylene glycol, also of monoethers of di- and tripropylene glycols, and also to isolate and identify some representatives of the latter. The reactions in question proceed according to the following scheme:



It is known that the reaction of propylene oxide with alcohols can go in the absence of catalysts but under rather drastic conditions; it is therefore usual to conduct this reaction in presence of catalysts; the latter can be substances of basic character (alkoxides of alkali metals, alkalies, tertiary amines), or of acidic character (sulfuric acid, boron trifluoride, etc.). On the basis of the considerations set forth below we selected an alkaline catalyst – sodium hydroxide.

Bearing in mind that the reaction of propylene oxide with alcohols at atmospheric pressure leads to formation almost exclusively of ethers of propylene glycol, we worked at higher pressures. It was established that the molecular weight of the reaction products depends in great measure upon the ratio of components: with increasing molar proportion of propylene oxide the content of ethers of di-, tri- and polypropylene glycols in the reaction product increases. With the objective of ascertaining the optimum ratio of components at which the highest yield of ethers of di- and tripropylene glycol is reached, experiments were run with one of the alcohols – isoamyl alcohol. The results of these experiments are set forth in Table 1; the composition of the reaction products was established by vacuum fractionation into fractions whose boiling limits correspond to the boiling points of ethers of mono-, di- and tripropylene glycol.

TABLE 1

Interaction of propylene oxide with isoamyl alcohol in various molar ratios

Experiment number	Starting substances (in moles)		Maximum temperature	Maximum pressure (in atm)	Fractions of reaction products (in %)				
					Boiling point				
	isoamyl alcohol	propylene oxide			up to 70° (20 mm)	70-90° (20 mm)	90° (20 mm) 115° (10 mm)	115° (10 mm) 205° (5 mm)	residue above 205° (5 mm)
1	1	1	170°	5.5	32.7	23.8	24.6	13.7	5.2
2	1	1.5	180	9	25.4	24.6	22.8	18.0	9.2
3	1	2	190	13	11.9	16.9	23.0	36.0	12.2
4	1	3	200	23	10.7	16.4	13.6	31.0	28.3

From Table 1 it is seen that an alcohol/oxide ratio of 1 : 2 is to be preferred, and we therefore used this ratio in experiments with other alcohols.

We studied the reaction of propylene oxide with isopropyl, n-butyl, isoamyl and cyclohexyl alcohols. Reaction conditions are given in Table 2.

TABLE 2

Reaction of alcohols with propylene oxide (oxide/alcohol molar ratio of 2:1)

Preparation No.	Alcohol	Max. temp.	Max. pressure (atm.)
1	Isopropyl	200°	25
2	n-Butyl	190	16
3	Isoamyl	190	13
4	Cyclohexyl	190	15

The isopropyl, n-butyl and isoamyl ethers of mono-, di- and tripropylene glycols and the cyclohexyl ether of propylene glycol were isolated from the reaction products by repeated fractional distillations in vacuum. Determinations of specific gravity and refractive index were made for all the substances mentioned. Molecular weights were found from the content of active hydrogen (method of Chugaev-Tserevitinov as modified by Terentyev) [6] or cryoscopically. In addition the previously undescribed compounds were identified in the form of the α-naphthylurethanes. Acetylation of the butyl ether of dipropylene glycol gave the corresponding acetate.

Concerning the structure of the products obtained, the existing literature data * made a strict proof unnecessary; we therefore limited ourselves to the iodoform test [7]; this gave a positive result with all the substances prepared, thus demonstrating the presence of a free secondary hydroxyl group.

EXPERIMENTAL **

Reaction of propylene oxide with isopropyl alcohol. The components together with 0.2% sodium hydroxide were charged into a steel ampoule fitted with a manometer and heated in a bath of Wood's alloy. Rise of temperature was at first accompanied by rising pressure, after which the pressure started to fall abruptly as a sign of the end of the reaction. The ampoule was cooled and the contents subjected to fractional distillation in vacuum from a Claisen flask with a dephlegmator. Three fractions were separated.

Propylene glycol isopropyl ether [I, R = $CH(CH_3)_2$]. B.p. 136-137° (751 mm), 48° (20 mm), d_4^{20} 0.8776, n_D^{20} 1.4098, MR_D 33.35. $C_6H_{14}O_2$. Calculated 33.02. Literature data [3]: B.p. 137-138°, $d_{15.6}^{20}$ 0.879, n_D^{20} 1.4070.

Dipropylene glycol isopropyl ether [II, R = $CH(CH_3)_2$]. B.p. 79° (10 mm), d_4^{20} 0.9150, n_D^{20} 1.4212, MR_D 48.88. $C_9H_{20}O_3$. Calculated 48.57.

Found %: C 60.89, 61.01; H 11.50, 11.12. $C_9H_{20}O_3$. Calculated %: C 61.33; H 11.44.

Tripropylene glycol isopropyl ether [III, R = $CH(CH_3)_2$]. B.p. 103-105° (3 mm), d_4^{20} 0.9392, n_D^{20} 1.4302, MR_D 64.47. $C_{12}H_{26}O_4$. Calculated 64.07.

Found %: C 61.08, 61.29; H 10.99, 11.33. $C_{12}H_{26}O_4$. Calculated %: C 61.50; H 11.18.

The substances described are colorless liquids with a faint odor; their viscosity increases appreciably with rising molecular weight; they are miscible in all proportions with alcohol and ether and are soluble in water.

Reaction of propylene oxide with butyl alcohol. The reaction was conducted under conditions similar to those for that with isopropyl alcohol. 3 fractions were isolated.

Propylene glycol butyl ether (I, R = n-C_4H_9). B.p. 71-72° (20 mm), d_4^{20} 0.8819, n_D^{20} 1.4184, MR_D 37.81. $C_7H_{16}O_2$. Calculated 37.70. Found M 127, 130; calculated 132.2. Literature data [3]: B.p. 74-74.5° (20 mm), $d_{15.6}^{20}$ 0.880, n_D^{20} 1.4170.

Dipropylene glycol butyl ether (II, R = n-C_4H_9). B.p. 103° (10 mm), d_4^{20} 0.9185, n_D^{20} 1.4278, MR_D 53.28. $C_{10}H_{22}O_3$. Calculated 53.19. Found: M 186; calculated 190.3.

The α-naphthylurethane of dipropylene glycol butyl ether was prepared by mixing equimolar amounts of the ether and α-naphthyl isocyanate in ligroine; the precipitate was washed several times with absolute alcohol; m.p. 265° (with decomp.).

Found %: N 4.17 (Kjeldahl). $C_{21}H_{29}O_4N$. Calculated %: N 3.89.

Dipropylene glycol butyl ether acetate. To 8.7 g of the ether with cooling and stirring was added from a dropping funnel 7.0 g acetyl chloride, the reaction mixture was heated on a boiling water bath for 2 hours, the excess of acetyl chloride was decomposed with cold water, and the organic layer was separated, washed with water, then with sodium carbonate solution and then again with water, dried over calcined magnesium sulfate and distilled in vacuum. Yield 8.2 g (77%). B.p. 119° (10 mm), d_4^{20} 0.9465, n_D^{20} 1.4230, MR_D 62.50. $C_{12}H_{24}O_4$. Calculated 62.56.

* When using an alkaline catalyst [2,3] the formation of only one of the possible isomers was established, namely the one that should give a positive result in the iodoform test.

** R. Ya. Belova collaborated in the experimental work.

Tripropylene glycol butyl ether (III, R = n-C_4H_9). B.p. 108-110° (3 mm), d_4^{20} 0.9365, n_D^{20} 1.4332, MR_D 68.93. $C_{13}H_{28}O_4$. Calculated 68.69.

α-Naphthylurethane, m.p. 250°. Found %: N 3.59 (Kjeldahl). $C_{24}H_{35}O_5N$. Calculated %: N 3.35.

The butyl ethers are colorless liquids, readily soluble in organic solvents but very much less soluble in water.

Reaction of propylene oxide with isoamyl alcohol. Three fractions were got under the above conditions (Table 2, item 3) after vacuum fractionation.

Propylene glycol isoamyl ether (I, R = iso-C_5H_{11}). B.p. 82-83° (20 mm), d_4^{20} 0.8718, n_D^{20} 1.4206, MR_D 42.49; calculated 42.32. Literature data [8]: B.p. 183.3°, d_{15}^{15} 0.8835, n_D^{25} 1.4182. Found: M 142, 141. $C_8H_{18}O_2$. Calculated: M 146.2.

Dipropylene glycol isoamyl ether (II, R = iso-C_5H_{11}). B.p. 108-109° (10 mm), d_4^{20} 0.9082, n_D^{20} 1.4298, MR_D 58.09; calculated 57.81.

Found: M 206. $C_{11}H_{24}O_3$. Calculated: M 204.3.

α-Naphthylurethane, m.p. 264° (with decomp.).

Found %: N 4.01 (Kjeldahl). $C_{22}H_{31}O_4N$. Calculated %: N 3.75.

Tripropylene glycol isoamyl ether (III, R = iso-C_5H_{11}). B.p. 113-115° (3 mm), d_4^{20} 0.9384, n_D^{20} 1.4354, MR_D 73.00. $C_{14}H_{30}O_4$. Calculated 73.31.

α-Naphthylurethane, m.p. 254-256° (with decomp.).

Found %: N 3.60 (Kjeldahl). $C_{25}H_{37}O_5N$. Calculated %: N 3.25.

The isoamyl ethers are colorless liquids with odor, readily soluble in organic solvents, poorly soluble in water.

Reaction of propylene oxide with cyclohexanol. Only the cyclohexyl ether of propylene glycol could be separated from the reaction products (I, R = C_6H_{11}), a colorless liquid with a faint pleasant odor, insoluble in water but soluble in organic solvents.

B.p. 105-106° (20 mm), d_4^{20} 0.9595, n_D^{20} 1.4557, MR_D 44.82; calculated 44.73. Found: M 156. $C_9H_{18}O_2$. Calculated M 158.3.

α-Naphthylurethane, m.p. 262° (with decomp.).

Found %: N 4.48 (Kjeldahl). $C_{20}H_{25}O_3N$. Calculated %: N 4.27.

SUMMARY

Reaction of propylene oxide with isopropyl, n-butyl, isoamyl and cyclohexyl alcohols under pressure in presence of sodium hydroxide gave the corresponding monoethers of mono-, di- and tripropylene glycols, 7 of which are described for the first time.

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SYNTHESIS OF KETONES BY THE ACTION OF ORGANOMAGNESIUM COMPOUNDS ON THE SODIUM SALTS OF CARBOXYLIC ACIDS

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On analyzing the known cases of preparation of tertiary alcohols from organomagnesium compounds [1], Yu. S. Zalkind arrived at the conclusion that the possibility of applying organomagnesium compounds to the preparation of ketones from acids or from their derivatives must be associated with a reduction in the reactivity of the carbonyl group of the acid [2]. He was the first to synthesize ketones by reacting dry salts of carboxylic acids [3] in the cold with an organomagnesium compound, and he obtained 25% yields of crude products; phenylisobutyl ketone, methyl isoamyl ketone, acetophenone and diethyl ketone were prepared [2].

Questions that arise are whether the method of preparation of ketones developed by Yu. S. Zalkind is a general one and whether the yield of ketones can be improved. These questions can only be answered by further experiments in this field. No other ketones, however, have been obtained by this route.

In the present work we aimed at preparing several other ketones by the action of organomagnesium compounds upon sodium salts of carboxylic acids and at studying the influence of varying conditions of synthesis upon the yield of ketones.

We have prepared ethyl phenyl ketone and ethyl heptadecyl ketone by the action of ethyl magnesium bromide upon the sodium salts of benzoic and stearic acids. The course of the synthesis of these ketones was of interest not only from the viewpoint of preparation of such ketones by a novel method but also for establishment of the possibility of using salts of aromatic acids, for example benzoic acid, for preparation of ketones with aromatic radicals. It also seemed of interest to ascertain whether the size of the acid radical influenced the yield of ketone, since from literature data it is known that the yield of ketones in their preparation by the action of organomagnesium compounds on acid amides is higher the higher the carbon content of the amide [4].

Our experiments, in conjunction with those previously carried out, support the view that the action of organomagnesium compounds on sodium salts of carboxylic acids is probably a general reaction, leading under specific conditions to formation of ketones; the reaction is also applicable to salts of aromatic acids. Concerning the yields of the ketones obtained, they vary considerably with the conditions of decomposition of the addition product.

EXPERIMENTAL

Preparation of ethyl phenyl ketone. 40 g solid sodium hydroxide was dissolved in 170 ml alcohol with stirring for 3 hours, and the solution of sodium alkoxide was gradually run into a solution of 120 g benzoic acid in 300 ml alcohol. The precipitated crystals of sodium benzoate were filtered, washed with ether, and dried to constant weight. Yield of salt 81%.

To ethyl magnesium bromide, prepared by the usual method from 6.4 g magnesium turnings and 20.5 g ethyl bromide, was gradually added (with external cooling of the reaction mixture with iced water) 38 g dry, finely pulverized sodium benzoate. After 24 hours (2-4 hours less makes little difference) the reaction product was decomposed with continuous stirring, at first with iced water and then with hydrochloric acid diluted with an equal volume of water. Study of the conditions of decomposition showed that 5% hydrochloric acid in general does not bring about decomposition, while the use of ammonium chloride (although possible) calls for subsequent use of hydrochloric acid. Use of 8 N sulfuric acid considerably lowers the yield of ketone.

The combined ethereal extracts (after decomposition and extraction with ether of the aqueous acid layer) were dried with anhydrous potassium carbonate and then distilled. Fractions were obtained with the following boiling ranges: 1) 60-103°; 2) 120-200°; 3) 212-218°. The residue in the distillation flask had a pungent, unpleasant odor.

The 3rd fraction quickly solidified in the side tube of the distillation flask and in the condenser; it had a characteristic odor and was insoluble in water. Yield 37%. According to the literature ethyl phenyl ketone has b. p. 214-216°, m. p. 18-20° [5]. The semicarbazone of ethyl phenyl ketone (light-yellow crystals) has m. p. 182-184° *.

* Literature data m. p. 182° [5].

Its 2, 4-dinitrophenylhydrazone was prepared as described by Shreiner and Fuson [6]. The red precipitate had m. p. 186° in agreement with the data in [5].

The products of the remaining fractions (obtained in very low yields) were not examined. It is possible that the product of the 2nd fraction is benzaldehyde since it has the same odor and crystallizes on lengthy standing; it is transformed into benzoic acid with m. p. 121°.

Preparation of ethyl heptadecyl ketone. 25 g stearic acid was dissolved with heating in 150 ml alcohol, and to the solution was added a solution of 3 g sodium hydroxide in 15 ml alcohol. The precipitated crystals of the sodium salt of stearic acid were filtered, washed with cold alcohol, and dried to constant weight. Yield of salt 92%.

Ethyl heptadecyl ketone was prepared similarly to ethyl phenyl ketone from 1.8 g magnesium. 8 ml ethyl bromide and 22 g sodium stearate. After crystallization from alcohol it had m. p. 59°. The literature gives 57-61° [5]. The prepared ethyl heptadecyl ketone dissolved in the cold in benzene and on heating in alcohol.

Ethyl heptadecyl ketoxime melts at 57° in agreement with the literature [5].

SUMMARY

1. Ethyl phenyl ketone can be prepared by the action of ethyl magnesium on dry sodium benzoate in a yield of up to 37%, which indicates the possibility of preparing from salts not only ketones of the aliphatic series but also ketones containing an aromatic radical.

2. Ethyl heptadecyl ketone can be obtained by the action of ethyl magnesium bromide on dry sodium stearate in a yield of up to 63%.

3. Comparison of the yields of various ketones obtained by the action of organomagnesium compounds on dry sodium salts of carboxylic acids [2] shows that the yield of ketone increases with increasing size of acid radical.

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REDUCTION WITH FORMIC ACID AND ITS DERIVATIVES

I. THE REDUCTION OF AZINES AND HYDRAZONES

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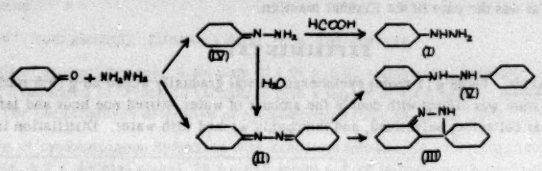
Interaction of cyclohexanone with ammonium formate, formamide or with formic acid and urea can lead to good yields, depending upon the conditions, of mono- or dicyclohexylamine [1]. Reaction of cyclohexanone with N-alkyl- or N-aryl formamide gives respectively N-alkyl- or N-arylcyclohexylamines [2]. It was of interest to proceed beyond the usual Leuckardt reaction and to investigate the reaction of N-aminoformamide (i. e. formyl hydrazine) or of hydrazine formate with carbonyl compounds. It was found that cyclohexanone with hydrazine hydrate and formic acid gives the expected cyclohexylhydrazine (I) only in insignificant yield (3-14%), the main mass being transformed into the azine (II) which then rearranges to 3, 4-tetramethylene-5, 5-pentamethylenepyrazoline (III).



The preferential formation of the azine instead of the hydrazone (IV) during the action of hydrazine hydrate on cyclohexanone was described by N. M. Kizhner [3]; it is likewise known that hydrazones are readily transformed into azines in presence of water [4].

Rearrangement of cyclohexanone azine to a pyrazoline base was previously observed by Stollé [5] on treatment with anhydrous oxalic acid. By heating cyclohexanone azine with formic acid, Robinson obtained a product which he believed to be a mixture of the formylated pyrazoline (III) and octahydrocarbazole [6].

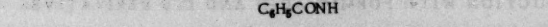
With the objective of suppressing the secondary formation of the pyrazoline base, we reduced the pure azine in less acidic media, i. e., using ammonium formate, formamide, triethylamine formate or a mixture of formic acid and sodium formate. Under these conditions the main product of the reaction (yield 89% when using triethylamine formate) was found to be N, N'-dicyclohexylhydrazine (V).

On reduction of the pure hydrazone with anhydrous formic acid, monocyclohexylhydrazine was obtained in 31% yield, while the remainder was transformed into the pyrazoline base (III) and dicyclohexylhydrazine.

On reduction of the acetylhydrazone of cyclohexanone with formic acid, a mixture of dicyclohexylhydrazine and base (III) was obtained. Consequently, the water present in the reaction medium and formed during decomposition of formic acid transforms the hydrazone into the azine and therefore cyclohexylhydrazine is not formed, while formic acid causes rearrangement of the azine, thus hindering its reduction which evidently proceeds at a very much lower speed.

We obtained N,N'-dicyclohexylhydrazine, after hydrolysis of the reaction mixture with hydrochloric acid, in the form of its dihydrochloride. The melting points of the dihydrochloride and of the phenylcarbamide derivative of the hydrazine agree with the literature data. However, the free base isolated from the dihydrochloride had m. p. 62° (the literature reports m. p. 6-10° for N,N'-dicyclohexylhydrazine distilled in a nitrogen stream [7]). Our hydrazine with m. p. 62° gave, after distillation in a stream of nitrogen, an oil that solidified at 0-2° and had constants similar to those in the literature. On vacuum distillation in a nitrogen stream an oil crystallizing at 15-20° was obtained.

For confirmation of the structure of the substance with m. p. 62° we performed the following series of reactions:



Since azocyclohexane and the dibenzoyl and benzaldehyde derivatives of cyclohexylhydrazine had constants similar to those reported in the literature, we are able to confirm that N,N'-dicyclohexylhydrazine has m. p. 62°, and not 6-10° as reported in the literature [7]. Thus, both the hydrazone and the azine of cyclohexanone on heating with formic acid (4-9 hours, 100-120°) are reduced to the corresponding hydrazines. The cyclic hydrazone (III), the phenylhydrazone of cyclohexanone, azobenzene, and the azines of benzaldehyde and acetophenone are not reduced under these conditions. The azines of butyraldehyde, acetone and cyclopentanone give mixtures of condensation products from which the hydrazines could not be isolated. The azines of pinacolone (3,3-dimethyl-2-butanone) and butyrone (4-heptanone) are substantially completely hydrolyzed (the original ketones are isolated). 15-hours' heating of benzophenone hydrazone with formamide (160°) gave diphenylmethane and benzophenone azine.

In this case the hydrazone evidently suffered decomposition in part with evolution of nitrogen, but not in the usual alkaline medium, as was the case in the Kizhner reaction.

EXPERIMENTAL

Cyclohexanone azine. To 98 g (1 mole) cyclohexanone was gradually added 26 g (0.5 mole) 96% hydrazine hydrate. The cooled mixture was diluted with double the amount of water, stirred one hour and left overnight at 0-5°. The precipitate was collected, pulverized, and thoroughly washed with water. Distillation in vacuum gave 90 g (93.7%) azine.

B. p. 143-150° (13 mm). After redistillation it had b. p. 147° (13 mm), 152° (15 mm), 167° (19 mm); n_D^{21} 1.5261, m. p. 35°.

Literature data: b. p. 156° (16 mm) [6], 175° (28 mm), n_D^{20} 1.5268, m. p. 33.5-34° [3], 35° [5], 37° [6].

Cyclohexanone hydrazone hydrate. To 150 g (1.5 moles) 50% hydrazine hydrate, with good stirring, was added in the course of 1.5 hours 48 g (0.5 mole) cyclohexanone, and the mixture allowed to stand 24 hours. After saturation of the mixture with potassium carbonate, the oily layer was separated and the aqueous layer extracted with ether; the oily layer and the ethereal extracts were dried with fused potassium carbonate and distilled in vacuum to give 23 g (35.4%) cyclohexanone hydrazone hydrate, b. p. 96-102° (24 mm), n_D^{21} 1.5088 (literature data: b. p. 107-108° at 28 mm [3]) and 25 g (52%) cyclohexanone azine: b. p. 156-158° (17 mm), n_D^{21} 1.5262.

N,N'-Dicyclohexylhydrazine dihydrochloride. a) To a mixture of 8.8 g (0.046 mole) cyclohexanone azine, 13.6 g (0.2 mole) sodium formate and 0.2 g skeletal nickel, heated to 150°, was added during 2 hours 20 g (approx. 0.3 mole) 75% formic acid; after 6-hours' refluxing, the upper oily layer was separated and the aqueous layer extracted with ether. The ethereal extracts and the oily layer were boiled (after removal of solvent) for 15 minutes with 30 ml concentrated hydrochloric acid, saturated with hydrogen chloride; the precipitated salt was filtered and dried. After dissolution in methanol it was brought down with concentrated hydrochloric acid and hydrogen chloride. M. p. 271° [7].

Found %: N 10.20. $C_{12}H_{26}N_2Cl_2$. Calculated %: N 10.41.

b) A mixture of 19.2 g (0.1 mole) azine, 30.5 g (0.5 mole) ammonium formate and 0.2 g skeletal nickel was refluxed 6 hours, diluted with twice the amount of water and extracted with benzene. The benzene was driven off and the residue boiled with 50 ml concentrated hydrochloric acid and saturated with hydrogen chloride. Yield 20.1 g (75.4%) of N,N'-dicyclohexylhydrazine with m. p. 267°.

c) A mixture of 19.2 g (0.1 mole) azine, 50.4 g (0.5 mole) triethylamine, 27 g (0.5 mole) 85% formic acid and 0.5 g skeletal nickel was refluxed 3 hours. Following this, addition was made for 7 hours at the boil of a further 10.8 g (0.2 mole) 85% formic acid. At the end of the reaction, addition was made of 50 ml benzene and 100 ml 5% hydrochloric acid; the benzene layer was separated and the aqueous layer extracted with benzene. Working in the usual manner gave 23.9 g (89%) dihydrochloride with m. p. 268°.

N,N'-dicyclohexylhydrazine base. 26.8 g (0.1 mole) N,N'-dicyclohexylhydrazine dihydrochloride was shaken in a separating funnel with 60 ml ether and 50 ml 15% ammonia solution. The ether layer was separated and dried with sodium. After evaporation of the ether the free base at once crystallized.

M. p. 62°. On distillation in a nitrogen stream the b. p. was 265-272° (768 mm), m. p. 0-2°, n_D^{20} 1.4994. On distillation in vacuum in a stream of nitrogen the b. p. was 150-158° (19 mm), m. p. 15-20°. Literature data: m. p. 6-10° [7], b. p. 220-260° [3], 260-270° (775 mm) [8], 260-270° (740 mm), n_D^{23} 1.4888 [7].

Dibenzoyl derivative m. p. 397° (in sealed capillary).

Found %: N 7.02. $C_{16}H_{22}O_2N_2$. Calculated %: N 6.93.

Diacetyl derivative m. p. 146°. Phenylcarbamide derivative m. p. 123° (from alcohol) [5].

Azocyclohexane. A solution of 5.82 g (0.03 mole) N,N'-dicyclohexylhydrazine in 50 ml dry ether was heated 1.5 hours with 12.98 g (0.06 mole) mercuric oxide. The ether was removed and the residue washed with ether. Evaporation of the ether from the ethereal extracts left 5.2 g (90%) azocyclohexane.

B. p. 140° (22 mm), m. p. 35°. Literature data: m. p. 32° [8], 34.5° [7].

Found %: N 14.48. $C_{12}H_{22}N_2$. Calculated %: N 14.44.

Reaction of azocyclohexane with benzoyl chloride. 3.88 g (0.02 mole) azocyclohexane and 8.4 g (0.06 mole) benzoyl chloride were shaken in 10% sodium hydroxide solution to give 6 g (93.5%) of the dibenzoyl derivative of cyclohexyhydrazine.

M. p. 194° (from alcohol). Literature data: m. p. 195-196° [9].

Hydrolysis of azocyclohexane. A mixture of 1.94 g (0.01 mole) azocyclohexane and 5 ml concentrated hydrochloric acid was evaporated to dryness in vacuum to give a residue of 1.4 g petroleum jelly-like cyclohexylhydrazine hydrochloride. The benzaldehyde derivative of cyclohexylhydrazine has m. p. 178° (from alcohol).

Reduction of cyclohexanone hydrazone with anhydrous formic acid. To 3.9 g (0.03 mole) cyclohexanone hydrazone hydrate, 0.2 g skeletal nickel, 13.6 g (0.2 mole) sodium formate and 1.8 g (0.03 mole) anhydrous formic acid was added at the boil, during 5 hours, 10.8 g (approx. 0.2 mole) anhydrous formic acid. After dilution with three times the amount of water, the oily layer was separated and the aqueous layer extracted with ether. The ethereal layers were hydrolyzed (after driving off the solvent) by boiling with 15 ml concentrated hydrochloric acid. Saturation of the solution with hydrogen chloride gave 2 g (49.5%) N,N'-dicyclohexylhydrazine dihydrochloride with m. p. 267°. The filtrate was made alkaline with solid alkali and extracted with ether. Fractionation of the extracts (dried with sodium sulfate) gave 1.1 g (31%) cyclohexylhydrazine.

B. p. 190-195° (751 mm), m. p. 44-47° [3]; benzaldehyde derivative m. p. 178° (from ethyl acetate) [7, 9]. Dibenzoyl derivative m. p. 195° (from alcohol); no melting point depression in mixed test with product from azocyclohexane.

Reaction of cyclohexanone with hydrazine hydrate and formic acid in presence of sodium formate. To 49.9 g (0.5 mole) cyclohexanone, 0.5 g skeletal nickel and 34 g (0.5 mole) sodium formate, heated to the boil, was added dropwise a mixture of 15 g (about 0.25 mole) 85% hydrazine hydrate and 41 g (about 0.8 mole) 85% formic acid. After 4-hours' heating at 120° the oily layer was collected and hydrolyzed by boiling with concentrated hydrochloric acid. A voluminous precipitate of N,N'-dicyclohexylhydrazine dihydrochloride came down and was filtered and washed with ether. Yield 31.5 g (46.3%) of N,N'-dicyclohexylhydrazine dihydrochloride with m. p. 266°.

The filtrate was evaporated in vacuum and the residual viscous oil was treated with caustic alkali and extracted with ether. After drying with fused sodium hydroxide, the extracts were fractionated to give 2 g (3.5%) cyclohexylhydrazine with b. p. 190-195° (750 mm); benzaldehyde derivative with m. p. 178° (from ethyl acetate), and 12 g (25%) 3,4-tetramethylene-5,5-pentamethylene-pyrazoline, b. p. 165-167° (15 mm), m. p. 60°; phenylcarbamide derivative, m. p. 122° (from alcohol) [5].

Literature data [5]: b. p. 165° (17 mm), m. p. 64°.

Reduction of benzophenone hydrazone. The hydrazone was prepared by heating 36.4 g (0.2 mole) benzophenone with 26 g (0.5 mole) 96% hydrazine hydrate for 6 hours under a reflux condenser. Quantitative yield, m. p. 98-99° [10].

A mixture of 19 g (0.1 mole) hydrazone, 30 g (about 0.6 mole) formamide, 0.5 g skeletal nickel and 13.6 g

(0.2 mole) sodium formate was heated 16 hours at a temperature of the mixture of 130-140°. The reaction mass was diluted with water and extracted with ether. The ethereal extract contained 10 g diphenylmethane, b. p. 256-261° (750 mm), m. p. 24-28°. In addition 5.8 g crystals with m. p. 161°, poorly soluble in ether, was obtained and was identified as benzophenone azine.

Literature data: m. p. 162° [9].

Reduction of the acetylhydrazone of cyclohexanone with formic acid. 9.8 g (0.1 mole) cyclohexanone was mixed with 7.4 g (0.1 mole) acetylhydrazine, and addition was made of 21 g (approx. 0.3 mole) ammonium formate and 0.5 g skeletal nickel before refluxing for 4 hours. The usual treatment gave 4.1 g (39.8%) dicyclohexylhydrazine dihydrochloride (m. p. 268° [8]) and 3.1 g (31.6%) pyrazoline base (III).

SUMMARY

1. It was shown that reaction of cyclohexanone with hydrazine and formic acid leads, in dependence on the conditions, to cyclohexyl- and dicyclohexyl- hydrazine or 3,4-tetramethylene-5,5-pentamethylenepyrazoline.

2. It was found that the formation of the pyrazoline base proceeds through the step of rearrangement of the azine of cyclohexanone under the influence of formic acid.

3. In contrast to azines of a series of other ketones, cyclohexanone azine under appropriate conditions is smoothly reduced by formic acid to dicyclohexylhydrazine.

4. A preparative method for obtaining dicyclohexylhydrazine in 80-90% yield is proposed.

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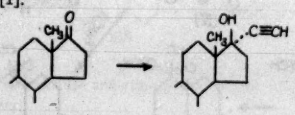
THE SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

XXX. THE STEREOCHEMISTRY OF THE ACETYLENE SYNTHESIS WITH BICYCLIC KETONES. HYDRATION OF BICYCLIC ACETYLENIC ALCOHOLS

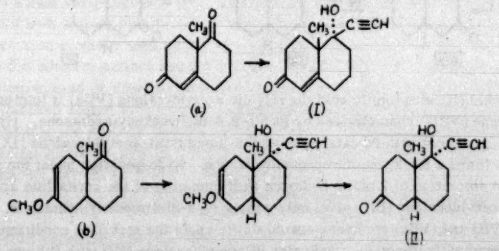
I. N. Nazarov and I. A. Gurvich

It is known that in 17-ketosteroids additions at the carbonyl group proceed as a rule with formation of 17β-hydroxy compounds. In particular the condensation of acetylene with 17-ketosteroids leads to formation of 17α-ethynyl-17β-hydroxy derivatives [1].



In the case of D-homosteroids the main product of reaction is likewise an acetylenic alcohol with a 17β-hydroxy group [2]. The spatial directivity of these reactions is governed by the neighboring angular methyl group and by the characteristics of the spatial structure of the steroid system.

As was shown in the preceding communications, the condensations of acetylene with substituted 9-methyl-1-octalones that have been studied in our laboratory likewise lead to specific but sterically opposite forms of acetylenic alcohols. Thus, in the condensation of 9-methyl-1, 6-diketo-Δ^5-octalin (a) with acetylides of the alkali metals, one crystalline alcohol (I) [3] is formed in 70% yield. Condensation of 9-methyl-6-methoxy-1-keto-Δ^6-octalin (b) with sodium acetylide gave, after hydrolysis, the acetylenic alcohol (II) [4] as the sole product.



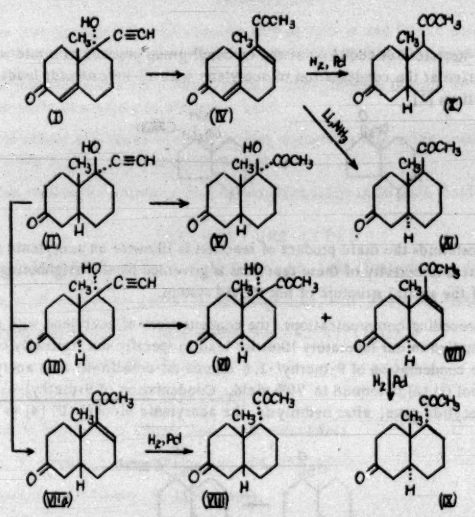
As we have previously shown [3], alcohols (I) and (II) contain substituents in opposed steric positions at the first carbon atom; this is due to the special features of the steric structure of the original octalones (a) and (b).

The problem of the actual steric configurations of alcohols (I) and (II) was solved by an investigation of their hydration and of the hydration of the trans-acetylenic alcohol (III) that we previously obtained by reduction of the double bond in alcohol (I). Thus, on hydration of acetylenic alcohol (II) in methanol solution in presence of mercuric sulfate, a 70% yield was obtained of acetyloxydecalone (V) which forms a bis-2, 4-dinitrophenylhydrazone.

Hydration of the acetylenic alcohol (I) under the same conditions at a temperature below 60° gave a single crystalline product which we succeeded in isolating and identifying as the acetylhexalone (IV); the latter forms a mono-2, 4-dinitrophenylhydrazone. The presence in the acetylhexalone (IV) of a double bond conjugated with the ketonic groups was proved by the ultraviolet absorption spectrum of both the acetylhexalone itself and of its 2, 4-dinitrophenylhydrazone. Whereas hydration of alcohols (I) and (II) is entirely completed in 7-8 hours, in the case

of hydration of the trans-acetylenic alcohol (III) the original product is recovered almost completely even after 10-hours boiling of the reaction mass under the same conditions. After 30-hours boiling the normal product of hydration (VI) could be isolated by chromatography together with a smaller amount of trans-acetyloctalone (VII). The diketone (VI) forms only a mono-2, 4-dinitrophenylhydrazone, whereas acetyloctalone (VII) gives a bis-2, 4-dinitrophenylhydrazone. Judging by the absorption spectrum, the latter contains a pyrazoline ring.

By heating alcohol (I) with formic acid we obtained two crystalline products, isomeric with the original alcohol (I) and diketone (IV), whose structure was not established. Mention is made in the literature of the preparation under these conditions of a crystalline substance, isomeric with alcohol (I), which the author erroneously assumed to be the diketone (IV) and which, judging by the reported melting point, is not a pure substance [5]. Other authors have likewise erroneously assumed the liquid mixture of substances to be diketone (IV) [6].

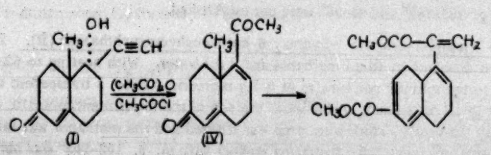


On heating alcohol (II) with formic acid the oily cis-acetyloctalone (VIIa) is formed, which on hydrogenation gives cis-acetyldecalone (VIII), characterized by its bis-2, 4-dinitrophenylhydrazone. Hydrogenation of trans-acetyloctalones (VII) in ethanol with Pd catalyst gives the liquid trans-acetyldecalone (IX) which, like the original acetyloctalone (VII), forms a bis-2, 4-dinitrophenylhydrazone. Hydrogenation under the same conditions of acetylhexalone (IV) leads to absorption of 2 moles hydrogen with formation of the crystalline acetyldecalone (X) which, unlike the isomeric acetyldecalone (IX), gives only a mono-2, 4-dinitrophenylhydrazone. It should be noted that the acetyloctalones (VII) and (VIIa) are hydrogenated slowly under the specified conditions, whereas acetylhexalone (IV) is hydrogenated extremely smoothly. Reduction of acetylhexalone (IV) with lithium in liquid ammonia gave the high-melting crystalline acetyldecalone (XI) which, like the isomeric acetyldecalone (X), forms only a mono-2,4-dinitrophenylhydrazone. Since cis-decalones are preferentially formed on catalytic hydrogenation of Δ^5-6-octalones while trans-decalones are formed on reduction with lithium in liquid ammonia [3], it can be assumed that acetyldecalone (X) belongs to the cis-decalin series, while the isomeric decalone (XI) is a derivative of trans-dicalin. The marked difference between the rates of hydration of acetylenic alcohols (II) and (III) and the facility of dehydration of acetylenic alcohols (III) and (I) in an acid medium (under conditions of hydration of the triple bond) are governed by the spatial structures of these alcohols. The only factor hindering the hydration of the triple bond in alcohol (III) can be the cis-position of the ethynyl group in relation to the angular methyl group in the system 1-ethynyl-9-methyldecalin. Consequently the hydroxyl group in alcohols (I) and (III) is in the trans-position to the angular methyl group and occupies, just like the latter, a polar position which, as is known, facilitates dehydration. The fact that diketones (VI), (X) and (XI) form only mono-dinitrophenylhydrazones also indicates a cis-position of the acetyl groups in these compounds in relation to the angular methyl groups, and this also creates

steric hindrances which influence the reactivity of the acetyl carbonyls. Conversely, with a trans-position of the acetyl chain in relation to the angular methyl group in diketones (V), (VIII) and (IX), the acetyl carbonyl reacts normally with 2, 4-dinitrophenylhydrazine and these diketones form bis-2, 4-dinitrophenylhydrazones.

Whereas acetyloctalone (VII) is hydrogenated to the acetyldecalone (IX) with a trans-acetyl group, hydrogenation of $\Delta^{1,5}$-acetylhexalone (IV) gives the acetyldecalone (X) with a cis-position of the acetyl chain. This difference in the direction of hydrogenation of the Δ^{1}-bond may possibly be due to it being hydrogenated in the acetylhexalone (IV) before the Δ^{5}-bond.

Reaction of acetic anhydride with the acetylenic alcohol (I) in presence of acetyl chloride at room temperature gives a crystalline substance whose analysis corresponds to that of the dienol acetate of the diketone (IV).



This compound is unstable to moisture and atmospheric oxygen, and even on gentle heating in ether it adds on oxygen and a molecule of water.

An attempt to dehydrate the diketo alcohol (V) with the help of potassium bisulfate led to formation of a high-melting substance of unstable structure, whose analysis was similar to that of the original substance. Treatment of the diketo alcohol (V) with thionyl chloride and pyridine led to simultaneous dehydration and oxidation. The crystalline product was not further investigated.

EXPERIMENTAL

Hydration of 9-methyl-1-ethynyl-1-hydroxy-6-keto-Δ^{5}-octahydronaphthalene (I). 4 g acetylenic alcohol (I) (m. p. 169-170°) was dissolved in 96 ml methanol and 8 ml water. Then, with heating to 56° and with stirring, addition was made to the solution portionwise of 1. 4 g finely pulverized mercuric sulfate. The reaction was conducted for 6. 5 hours at a bath temperature of 60°. The next day the colored solution was filtered from metallic mercury and neutralized with sodium bicarbonate; the methanol was distilled off in vacuum; water was added to the residue, and the reaction products were extracted with ether and chloroform. Both extracts were dried with sodium sulfate. From the ethereal extract was got 3 g dark oil, and from the chloroform extract 1. 2 g oil. Both fractions were chromatogrammed on alumina and were eluted with benzene, ether, chloroform, acetone and methanol. From the fractions eluted with ether and chloroform was isolated in all 0. 85 g crystals with m. p. about 120°. On prolonged standing the acetone fraction yielded a further 0. 15 g of the same crystals. Recrystallization from ether gave a colorless substance with m. p. 122-123° — 9-methyl-1-acetyl-6-keto-$\Delta^{1,5}$-hexahydronaphthalene (IV). $\lambda_{max.}$ (in methanol) 257 mμ (ε 10900), 315 mμ (ε 112.5).

Found %: C 76. 70, 76. 67; H 8. 00, 8. 13. $C_{13}H_{16}O_2$. Calculated %: C 76. 43; H 7. 90.

The mono-2, 4-dinitrophenylhydrazone of the diketone (IV) forms dark-red crystals with m. p. 218. 5 - 219. 5° $\lambda_{max.}$ (in methanol) 388 mμ.

Found %: C 59. 45, 59. 34; H 5. 49, 5. 59. $C_{19}H_{20}O_5N_4$. Calculated %: C 59. 36; H 5. 35.

A mixed sample with the isomeric 2, 4-dinitrophenylhydrazone of the original acetylenic alcohol (I) (m. p. 217-218°) melted at 203-204° after softening at 197°. Non-crystalline resins separated from the benzene and methanol fractions.

Isomerization of the acetylenic alcohol (I) with formic acid. A solution of 1 g of the acetylenic alcohol (I) in 10 ml 91% formic acid was heated for 1 hour 10 minutes at a bath temperature of about 120°. The solution acquired a dark-cherry color. The formic acid was distilled off in vacuum. To the residue was added 4 ml water and the product was extracted with ether. The ether extract was neutralized with sodium carbonate, washed with water and dried with magnesium sulfate. Removal of the ether left 740 mg substance. Addition of benzene brought down 340 mg crystals with m. p. 144-155° which could not be separated by crystallization into individual compounds. Chromatogramming of the acetone fraction and mechanical sorting and crystallization of the ethyl acetate

fraction gave the original alcohol (I) with m. p. 170-171° and a substance isomeric with the original alcohol with m. p. 181-182°.

Found %: C 76.35, 76.62; H 8.02, 8.18. $C_{13}H_{18}O_2$. Calculated %: 76.43; H 7.90.

A mixture with the original alcohol (I) melted at 147-152°.

After chromatography of the benzene solution from the ether fraction, crystals were isolated which after a second chromatography melted at 95-96°.

Found %: C 76.70; H 7.68. $C_{13}H_{18}O_2$. Calculated %: C 76.43; H 7.90.

The original alcohol (I) was separated from the chloroform fraction. From the acetone fraction was obtained a mixture of crystals of the original alcohol and the above-described substance with m. p. 181°. The structures of the compounds with m. p. 181-182° and 95-96° were not established.

Hydration of cis-9-methyl-1-ethynyl-1-hydroxy-6-ketodecahydronaphthalene (II). 2 g acetylenic alcohol (II) (m. p. 157-158°) was dissolved in 48 ml methanol and 4 ml water. With heating to 63-65° and with stirring, addition was then made to the solution portionwise of 0.7 g mercuric sulfate; a transparent solution was formed. Reaction was carried out in all for 8 hours, and toward the end of the experiment metallic mercury began to come down. The following day the nearly colorless solution was filtered and the methanol was taken off in vacuum. After working up in the usual manner, 1.6 g hydration product with m. p. 102-103° was obtained. Two crystallizations from benzene + ligroine gave cis-9-methyl-1-acetyl-1-hydroxy-6-ketodecahydronaphthalene with m. p. 110-111°.

Found %: C 69.89, 69.69; H 8.89, 8.84. $C_{13}H_{20}O_3$. Calculated %: C 69.61; H 8.97.

The bis-2,4-dinitrophenylhydrazone forms orange crystals with m. p. 235-236°.

Found %: N 18.77, 18.59. $C_{25}H_{28}O_9N_8$. Calculated %: N 19.27.

Isomerization of the acetylenic alcohol (II). 1.4 g acetylenic alcohol (II) was heated in 12 ml 85% formic acid for 1 hour 10 minutes at a bath temperature of about 120°. The solution acquired a cherry color. The formic acid was distilled off in the vacuum of a water jet pump. To the residue was added 6 ml water and the product was extracted with benzene. The benzene extract was neutralized with sodium carbonate solution, washed with water and dried with sodium sulfate. The benzene solution was chromatogrammed over alumina. From the benzene fraction was obtained 830 mg oil. A second chromatogramming gave 660 mg oil which was exhaustively hydrogenated in alcohol solution in presence of Pd catalyst; about 80 ml hydrogen was absorbed in this step. After chromatogramming, the benzene fraction yielded 5 mg oily acetyldecalone (VIII). The orange bis-2,4-dinitrophenylhydrazone of this diketone melts at 219-220° (after boiling in ethyl acetate) $\lambda_{max.}$ 365 mμ (in methanol).

Found %: C 52.93, 52.97; H 5.15, 5.12. $C_{25}H_{28}O_8N_8$. Calculated %: C 52.81; H 4.96.

The original alcohol (II) was obtained from the acetone fraction.

Hydration of trans-9-methyl-1-ethynyl-1-hydroxy-6-ketodecahydronaphthalene (III). A mixture of 1.2 g acetylenic alcohol (III) (m. p. 155-156°), 29 ml methanol, 3 ml water and 0.36 g mercuric sulfate was stirred at a bath temperature of 63-67° for 9 hours. After working up, mainly the original product (mixed melting test) was isolated. The recovered alcohol (III) was dissolved in 80 ml methanol and 7 ml water and 1 g mercuric sulfate were added. The mixture was then stirred at 69-71° for 19 hours. By chromatography from the benzene fraction was then obtained 140 mg trans-9-methyl-1-acetyl-6-keto-Δ^5-octahydronaphthalene (VII) with m. p. 106-107°; two crystallizations from ether brought the melting point to 109-109.5°. $\lambda_{max.}$ 232 mμ (ϵ 9300), 303 mμ (ϵ 43) (in methanol).

Found %: C 75.49, 75.62; H 8.80, 8.71. $C_{13}H_{18}O_2$. Calculated %: C 75.69; H 8.80.

The orange bis-2,4-dinitrophenylhydrazone, after boiling ethyl acetate, melts at 225-226°. $\lambda_{max.}$ 365 mμ (in methanol).

Found %: N 19.18, 19.09. $C_{25}H_{28}O_8N_8$. Calculated %: N 19.78.

From the chloroform fraction was isolated 0.2 g trans-9-methyl-1-acetyl-1-hydroxy-6-ketodecahydronaphthalene (VI) with m. p. 147-148° (from benzene).

Found %: C 69.53, 69.50; H 8.99, 9.05. $C_{13}H_{20}O_3$. Calculated %: C 69.61; H 8.97.

A mixed specimen with the original alcohol (III) starts to soften at 126° and melts at about 140°. (The ether fraction contains mainly the same alcohol). The yellow 2, 4-dinitrophenylhydrazone has m. p. 234-235° after two crystallizations from ethyl acetate. $\lambda_{max.}$ 363 mμ (in methanol).

Found %: N 14.03, 14.08. $C_{19}H_{24}O_5N_4$. Calculated %: N 13.85.

Hydrogenation of acetylhexalone (IV). 350 mg acetylhexalone (IV) was hydrogenated in 8 ml alcohol with Pd catalyst on calcium carbonate. In the course of 4 hours 88 ml hydrogen was absorbed (2 moles), and hydrogenation then ceased completely. There was obtained 9-methyl-1-acetyl-6-ketodecahydronaphthalene (X) with m. p. 116.5-117.5° (after three crystallizations from a mixture of benzene and ligroine).

Found %: C 75.04, 74.89; H 9.72, 9.76. $C_{13}H_{20}O_2$. Calculated %: C 74.96; H 9.68.

The orange 2, 4-dinitrophenylhydrazone of acetyldecalone (X) melts at 224-225°. $\lambda_{max.}$ 363 mμ (in methanol).

Found %: N 14.03, 13.97. $C_{19}H_{24}O_5N_4$. Calculated %: N 14.43.

Hydrogenation of acetyloctalone (VII). 130 mg acetylhexalone (VII) was hydrogenated in 11 ml alcohol with Pd catalyst; during the process about 25 ml hydrogen was absorbed and the hydrogenation then ceased. There was obtained 110 mg trans-9-methyl-1-acetyl-6-ketodecahydronaphthalene (IX) in the form of an oil; the bis-2, 4-dinitrophenylhydrazone of the latter has an orange color and melts at 232-233° (after boiling in ethyl acetate). $\lambda_{max.}$ 363 mμ (in methanol).

Found %: N 19.86, 19.64. $C_{25}H_{28}O_8N_8$. Calculated %: N 19.71.

Reduction of acetylhexalone (IV) with lithium in liquid ammonia. Into a solution of 0.5 g lithium in 170 ml liquid ammonia was run a solution of 0.6 g diketone (IV) in 75 ml anhydrous ether. Portionwise introduction was then made of a further 0.8 g lithium and 20 ml alcohol. The product was worked up on the same day. From the ether solution was obtained 0.5 g oil with traces of crystals; it was oxidized with 0.3 g chromic oxide in acetic acid. The usual treatment gave 0.34 g oil which was chromatogrammed; from 60 mg chloroform fraction was obtained a bis-2, 4-dinitrophenylhydrazone with m. p. 239-240°. λ 371 mμ (in methanol).

Found %: N 20.57. $C_{25}H_{26}O_8N_8$. Calculated %: N 19.78.

From the acetone fractions was isolated 9-methyl-1-acetyl-6-ketodecahydronaphthalene (XI) with m. p. 243-244° after softening at 237°.

Found %: C 75.31; H 9.71. $C_{13}H_{20}O_2$. Calculated %: C 74.96; H 9.68.

The yellow 2, 4-dinitrophenylhydrazone of acetyldecalone (XI) melts at 213-214°. λ 363 mμ (in methanol).

Found %: N 14.43, 14.51, 14.28. $C_{19}H_{24}O_5N_4$. Calculated %: N 14.43.

Acetylation of alcohol (I). A mixture of 0.5 g acetylenic alcohol (I), 0.4 ml acetyl chloride, 0.45 ml freshly distilled diethylaniline and 2 ml acetic anhydride was left in a closed flask for 3 days at room temperature; the acetylenic alcohol went wholly into solution (the reaction does not go in the absence of acetic anhydride). The solution was run into iced water and the product extracted with ether; the ethereal extract was washed with dilute sulfuric acid with sodium bicarbonate solution, and with water, and dried with magnesium sulfate. After chromatogramming, the benzene fraction yielded about 400 mg crystals with m. p. 86-92°.

Found %: C 70.59, 70.49; H 6.63, 6.68. $C_{17}H_{20}O_4$. Calculated %: C 70.81; H 6.68.

Dissolution of this substance in aqueous acetone resulted in formation of an oil. Crystallization from a mixture of ether and ligroine gave an ether-insoluble, colorless powder with m. p. 151-152°.

Found %: C 63.22, 63.04; H 6.80, 6.89. $C_{17}H_{22}O_6$. Calculated %: C 63.38; H 6.88.

Dehydration of the hydroxydiketone (V). a) 0.4 g hydroxydiketone (V) (m. p. 110-111°) was dissolved in a mixture of 3.5 ml dry pyridine and 5 ml ether. To the solution at −7° was added 0.9 ml freshly distilled thionyl chloride; a precipitate came down immediately. After standing 20 minutes in ice and 1 hour at room temperature, the reaction mass was poured into water and the product extracted with ether. The ethereal extract was washed with dilute acid, with water, with sodium carbonate and again with water, and dried with magnesium sulfate. Crystals were got with m. p. 201-202° (from benzene and ligroine and from aqueous acetone). The substance does not give a reaction for a double bond with bromine; it does not contain halogen or sulfur.

Found %: C 65.53, 65.14; H 7.85, 7.81. $C_{19}H_{18}O_4$. Calculated %: C 65.53; H 7.61.

From the mother liquor was separated about 100 mg of the original product.

b) A mixture of 1 g hydroxydiketone (V), 1 ml xylene and 0.4 g potassium bisulfate was heated in the vacuum of a water jet pump in presence of pyrogallol at 135-140°, while the xylene gradually distilled off. The flask was cooled and ether and water were added. The ethereal extract was washed with sodium carbonate solution and with water and dried with sodium sulfate. Crystallization from benzene + ligroine gave about 400 mg of the original hydroxydiketone (V). (No depression in mixed melting test.) From the mother liquor was obtained about 400 mg crystals which after three crystallizations from aqueous acetone and drying over phosphorus pentoxide melted at 201-202° and corresponded in analysis to the original hydroxydiketone (V). The structure of the prepared substance was not established.

SUMMARY

Hydration was carried out of the bicyclic acetylenic alcohols (I), (II) and (III) with formation of the corresponding normal products of hydration (V) and (VI) and of the unsaturated diketones (IV) and (VII). It was shown that in the acetylenic alcohols (I) and (III) the ethynyl chain is in the cis-position in relation to the angular methyl group, and the hydroxyl group is in the trans-position, whereas the acetylenic alcohol (II) has these substituents in the reverse positions. Due to the cis-position of the ethynyl chain in relation to the angular methyl group, the aceylenic alcohol (III) is hydrogenated with more difficulty (steric hindrance). For the same reason the acetyldecalones (VI), (X) and (XI) form only mono-2, 4-dinitrophenylhydrazones, since the cis-acetyl group, which is affected by the steric impediments, does not participate in this reaction. The acetyldecalones (V), (VIII) and (IX), containing the acetyl chain in the trans-position, readily give bis-2, 4-dinitrophenylhydrazones.

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THE SULFONATION REACTION

XXXVI. CONCERNING THE SULFONATING ACTIVITY OF OLEUM

A. A. Spryskov

Although oleum or fuming sulfuric acid is a widely employed sulfonating agent, no studies have hitherto been published on the sulfonating activity of oleum in a wide range of concentrations. Thus in a paper by Martinsen [1], measurements are reported of the rate of sulfonation with 2.4% oleum and with sulfuric acid. Lauer and Oda [2] studied the kinetics of sulfonation of anthraquinone in oleum and found that the reaction velocity increases with rising concentration of free sulfur trioxide to 3-5%, then falls, but starts to rise again at an oleum concentration of 10%. Cowdrey and Davis [3] determined the velocity constants of the sulfonation of p-nitrotoluene with oleum containing up to 8% free sulfur trioxide. Brand [4] determined the velocity constants of sulfonation of a series of aromatic compounds with oleum containing from 0.75 to 33% free sulfur trioxide. He showed that the sulfonating activity of oleum increases continuously with rising content of sulfur trioxide. Our experiments [5] showed that 55% oleum is more active than 73% oleum and considerably more active than free sulfur trioxide.

The present research was undertaken with the objective of studying the sulfonating activity of oleum in the range between low concentrations and 100% sulfur trioxide.

EXPERIMENTAL

1, 3, 5-Naphthalene trisulfochloride was chosen for the experiments because under the action of oleum it undergoes sulfonation with a velocity convenient for measurements and forms only the tetrasulfonic acid without such byproducts as sulfones and resins. Moreover in oleum at 125° the possibility of isomerization of the 1, 3, 5-trisulfonic acid is excluded.

Experiments were performed in the following manner. A weighed amount (0.8 g) 1, 3, 5-naphthalene trisulfochloride with m. p. 146° was dissolved in a weighed amount of oleum of definite concentration in a test tube which was then sealed and heated for 4 hours at 125 ± 0.5°. Heating from 107 to 125° took 15 minutes. The test tube was then opened, 20 ml distilled chlorosulfonic acid was added, and the mass heated 2 hours at 100° to convert the sulfonic acids into acid chlorides; on cooling the mass was poured on to ice. The mixture of tri- and tetrasulfochlorides was filtered off and dried in a vacuum desiccator over potassium hydroxide at room temperature. The amount of trisulfo derivative sulfonated to the 1, 3, 5, 7-tetrasulfonic acid was determined by the previously described method [6].

Since the active sulfonating forms of oleum are unknown to us, one series of experiments was performed with a constant amount of oleum and a second series with a constant amount of free sulfur trioxide. In the first series each 0.8 g 1, 3, 5-naphthalene trisulfochloride was treated with 9 g oleum containing 9 to 68% free sulfur trioxide. In these experiments each mole of trichloride corresponded to 5.4 to 41 moles free sulfur trioxide. In the second series addition was made to 0.8 g trichloride of that amount of oleum which contained, per mole of trichloride, about 15 moles free sulfur trioxide with a content of the latter of 10 to 100%. Thus in the process of sulfonation the concentration of free sulfur trioxide scarcely varied.

The experimental results, plotted in Fig. 1, show that in both series of experiments the activity of the oleum rises with increasing content of free sulfur trioxide, reaches a maximum, and then declines. In the first series of experiments the maximum corresponds to approximately 37-38% oleum, while in the second series it corresponds to 35% oleum. In the experiments corresponding to the descending branch of curve I, more trichloride was sulfonated than in the experiments of series II at identical concentrations of oleum taken, since the excess of oleum in those experiments of series I was greater than in the experiments of series II.

On comparing the amount of trichloride sulfonated by oleum and by sulfur trioxide, we can see that the velocity of sulfonation with 30-40% oleum many times exceeds the velocity of sulfonation with sulfur trioxide.

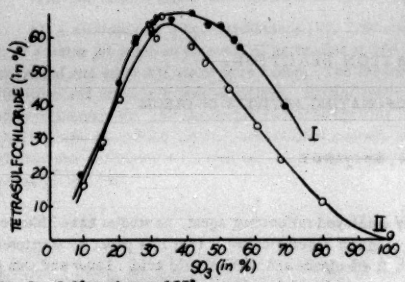

Fig. 1. Sulfonation at 125°.
I) first series of experiments; II) second series.

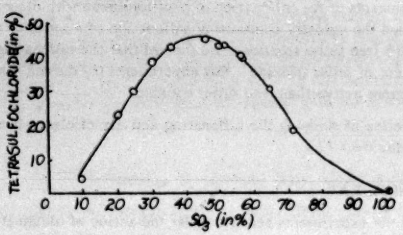

Fig. 2. Sulfonation at 84°.

In the experiments described, the sulfonation reaction proceeds at a temperature above the boiling point of oleum of high concentrations (26% and upwards); therefore a portion of the sulfur trioxide is present in the vapor phase and the composition of the liquid phase, in which the sulfonation takes place, varies somewhat. In order to study the influence of temperature upon the character of the curves representing the sulfonating activity of oleum, a third series of sulfonation experiments was run at 84°, i. e., at a temperature below the boiling point of oleum containing up to 48% free sulfur trioxide. The experiments were performed as described above except that sulfonation was carried out for 100 hours. The results of the experiments (Fig. 2) show that with falling temperature the character of the sulfonating activity of oleum of various concentrations hardly varies: the maximum is somewhat broadened and is shifted to 42-43% oleum.

It was earlier shown [5] that sulfur trioxide is more active than 100% sulfuric acid, while the results of the present investigation showed that 9% oleum is more active than sulfur trioxide. Consequently the activity of sulfur trioxide is equal to the activity of oleum with a content of free sulfur trioxide ranging from 0 to 9%. In the present investigation, however, it was impossible for us to establish precisely which concentration of oleum has the same sulfonating activity as sulfur trioxide.

EVALUATION OF RESULTS

In recent years a number of authors [3, 4, 7] have suggested that the sulfonating form is the SO_3H^+ ion.

A more probable process of ionization in oleum is the transfer of a proton from the very strong pyrosulfuric acid to sulfuric acid or to sulfur trioxide functioning as bases, i. e.

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-$$

$$H_2S_2O_7 + SO_3 \rightleftharpoons HSO_3^+ + HS_2O_7^- .$$

The pyrosulfuric/sulfuric acids molar ratio corresponds to 29% oleum, and the pyrosulfuric acid/sulfur trioxide molar ratio to 62% oleum. A rise in the concentration of free sulfur trioxide in oleum, starting from zero, will promote a shift of both equilibrium reactions to the right to a certain maximum, after which a rise of the sulfur trioxide content will lead to binding of the sulfuric acid (first equation) and to a fall in the relative amount of pyrosulfuric acid (second equation). These more favorable conditions for formation of ions are reached for the first equilibrium at a sulfur trioxide concentration very much lower than for the second equilibrium.

It is known that when sulfur trioxide dissolves in sulfuric acid, the electrical conductivity of the solution rises to a certain maximum and then falls sharply. The maximum of electrical conductivity lies at 9-16% oleum [8]. If a correction is made for viscosity, then the maximum is shifted to 16-20% oleum. Consequently ionization in oleum of high concentrations (45% and higher) proceeds according to the second equation since the free sulfuric acid content of the mixture remains very small and, judging by the electrical conductivity, occurs to a very small extent; we should therefore assume that it cannot dominate either in oleum of low or of medium concentrations. There are no grounds for stating that in oleum the SO_3H^+ ion is not formed or does not sulfonate; on the basis, however, of the results obtained and of the foregoing considerations, we are inclined to assume that in oleum of low and medium concentrations the predominant sulfonating form is the $H_3SO_4^+$ ion.

Oleum of high concentrations does not contain $H_3SO_4^+$ ions, or only a few, due to which its activity is lower.

P. T. Pestova participated in the investigation.

SUMMARY

The sulfonating activity of sulfur trioxide and oleum containing 9 to 80% free sulfur trioxide was studied at 84 and 125° with reference to the sulfonation of 1, 3, 5-naphthalene trisulfochloride, using various ratios of components.

It was found that with increasing content of free sulfur trioxide the sulfonating activity of oleum rises to a certain maximum (35-42%) and then declines.

The predominant sulfonating form in oleum of low and medium concentrations is apparently the $H_3SO_4^+$ ion.

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THE STRUCTURE AND PROPERTIES OF DIMETAL COMPOUNDS OF AZOMETHINES

I. STRUCTURE OF METALLIC COMPOUNDS OF AZOMETHINES

B. M. Mikhailov and K. N. Kurdyumova

On the basis of our investigations, which revealed the complex nature of diverse types of organic compounds of the alkali metals [1], it was natural to assume that also dimetal compounds of anils are complex compounds; we were therefore doubtful about the accuracy of the results of Schlenk and co-workers [2, 3] according to whom the dimetal compounds of anils, investigated by them with reference to disodium-benzophenone anil, do not contain a combined ether grouping, and we have therefore undertaken a study of the composition and structure of this class of substances.

We analyzed the product of addition of sodium to benzophenone anil not only for its content of metal but also for anil, and we established the error of Schlenk's conclusion about the composition of the compound investigated. It was actually found that its metal content is only a little more than 12%, while the anil content is not 85%, as would have been expected for compound (I) $(C_6H_5)_2CNa-NNaC_6H_5$, but only 67%. The difference of 20-21% on the average relates to combined ether in complex combination whose amount, in the case of a compound of one molecule with one molecule of anil, would theoretically be 19.62%.

The complex character of alkali organic compounds of azomethines was also detected during an investigation of other representatives of this class of substances. It was found, namely, that dilithium compounds of benzophenone-phenylimide and benzophenone-p-tolylimide and disodium compounds of benzophenone-o-tolylimide and benzophenone-p-tolylimide likewise contain a molecule of ether, while the dilithium compounds of benzophenone-o-tolylimide contain two molecules of combined ether (Table 1).

TABLE 1

Etherates	Found %			Calculated for etherate (%)		
	anil	metal	ether (by difference)	anil	metal	ether
$(C_6H_5)_2C=NC_6H_5 \cdot 2Li \cdot C_4H_{10}O$	69.46	4.16	26.38	74.52	4.02	21.46
$(C_6H_5)_2C=N \cdot C_6H_5 \cdot 2Na \cdot C_4H_{10}O$	67.00	12.27	20.73	68.19	12.19	19.62
$(C_6H_5)_2C=N-C_6H_3(CH_3)_2 \cdot 2Li \cdot 2C_4H_{10}O$	62.87	3.55	33.58	62.60	3.20	34.20
$(C_6H_5)_2C=N-C_6H_3(CH_3)_2 \cdot 2Na \cdot C_4H_{10}O$	68.18	11.57	20.26	69.32	11.75	18.94
$(C_6H_5)_2C=N-C_6H_4-CH_3 \cdot 2Li \cdot C_4H_{10}O$	71.66	4.14	24.24	75.51	3.86	20.65
$(C_6H_5)_2C=N-C_6H_4-CH_3 \cdot 2Na \cdot C_4H_{10}O$	68.36	11.11	20.55	69.32	11.75	18.94

For direct proof of the presence of ether in the dimetal compounds of azomethines, one of them (dilithium-benzophenone-p-tolylimide as the compound least soluble in ether) was isolated in the pure state in large amount and decomposed with water in the form of a suspension in benzene. Diethyl ether was found among the products of hydrolysis.

Regarding the structure of the disodium compounds of the anils, Schlenk adhered to the view that the atoms of metal in them are covalently bound to the atoms of nitrogen and carbon. We approached the problem of the nature of the bonds of the metals in the dimetal compounds of anils by studying their electrical conductivity. For this purpose we made use of an apparatus that we had constructed for ionophoresis of organic compounds of the alkali metals, employing 400-1000 d-c volts. The admissibility of determination of electrical conductivity in non-aqueous solutions with direct current was demonstrated for triphenylmethylsodium, the electrical conductivity of which under the usual conditions of measurement has been described in the literature [4]. Data for the electrical conductivity of triphenylmethylsodium obtained by various measuring methods are very similar (Table 2).

A study of the alkali organic compounds of azomethines showed that all of them, with exception of disodium-benzophenoneanil etherate, possess an electrical conductivity very similar to that of triphenylmethylsodium at a dilution of about 0.1 M, while at high dilution (molar volume 130-170) their electrical conductivity is nearly equal to that of triphenylmethylsodium (Table 2).

TABLE 2

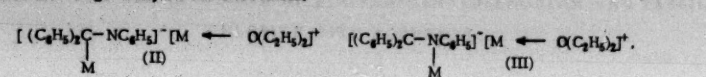
Electrical conductivity of ether solutions of organometallic compounds of anils

Name of compound	Molar volume			Specific electrical conductivity ($\cdot 10^{-6}$)			Molar electrical conductivity ($\cdot 10^{-2}$)		
	Experiment			Experiment			Experiment		
	1	2	3	1	2	3	1	2	3
Triphenylmethylsodium (our data)	13.87	42.40	129.1	5.620	39.600	4.8	7.80	1.680	0.61
Triphenylmethylsodium [4]	13.87	42.40	129.1	5.260	30.700	4.7	7.30	1.300	0.58
Dilithium-benzophenone anil etherate	10.00	50.00	188.1	2.640	0.220	0.0277	2.64	1.100	0.522
Disodium-benzophenone anil etherate	21.87	48.10	146.7	0.109	0.054	0.0262	0.239	0.264	0.384
Dilithium-benzophenone-o-tolylimide etherate	10.00	57.90	166.7	4.290	0.280	0.0416	4.29	1.600	0.690
Disodium-benzophenone-o-tolylimide etherate	–	52.17	182.9	–	0.075	0.0274	–	0.393	0.510
Dilithium-benzophenone-p-tolylimide etherate	10.10	49.56	140.0	4.010	0.688	0.0411	4.05	3.270	0.570
Disodium-benzophenone-p-tolylimide etherate	9.29	51.3	156.4	0.336	0.046	0.0205	2.98	0.236	0.320

The question as to whether the electrical conductivity of metal compounds of anils is associated with the ionized state of both atoms of metal or only of one of them can be answered on the basis of the following considerations. On the assumption that both atoms of metal in the monoetherates are in the ionized state, two structural variants are possible: either both of the metal ions are linked to one molecule of ether or one ion is coordinatively bound to the molecule of ether while the second ion is not bound to ether. The first variant is improbable because the tetravalent doubly-charged-positive state of oxygen, resulting from addition of two cations to ether, is energetically extremely unfavorable [5]; the second variant must also be rejected because in this case identical ions of metal prove to be non-equivalent in respect of ability to link with ether. We are therefore left with the assumption that in dimetal compounds of anils only one atom is in the ionized form, while one atom is covalently linked to the anion of the anil; proof is thus obtained of the non-equivalence of the metal atoms in respect to the coordinative addition of ether. This conclusion is supported by the structure of aminates of alkali organic compounds [6] containing only one molecule of tertiary amine and in which the addition of two cations to the onium is formally excluded.

Concerning the localization of the molecule of ether, there is no doubt that the ether is linked to the ionized solvated atom of the metal and not to the atom of metal forming the covalent bond.

Consequently, we must assign to the etherates of dimetal compounds of azomethines the structure (II) or (III), which differ in the position of the metal in the anion. Since nitrogen is more electronegative than carbon, structure (II) must be energetically the more favorable.



EXPERIMENTAL

Preparation of lithium and sodium complexes of compounds of anils and their analysis. All manipulations during preparation and analysis of lithium and sodium compounds of anils were performed in an atmosphere of dry nitrogen. Two-branch ampoules served as reaction vessels.

0.01 mole anil, 20-30 ml anhydrous ether, 0.03 g-atom alkali metal and glass beads were placed in an ampoule. The latter was sealed and shaken 50-60 hours. 30 ml ether was taken in the experiments with etherates of dilithium-benzophenone-phenylamide and disodium-benzophenone-phenylamide; in other cases 20 ml solvent was taken. The lithium and sodium complex compounds of anils obtained in this manner came down from solution in the form of finely crystalline and colored precipitates. Filtration and analysis of the complex compounds of anils were effected by the previously described procedure [6]. Experimental results are set forth in Table 1.

Determination of electrical conductivity. Use was made of a cell consisting of two cylindrical tubes joined by a crosspiece. The electrodes were platinum discs with a surface of 1 cm^2. The distance between the electrodes was 4 cm. The capacity of the cell was determined by the usual method (20°, 12.775). All operations were conducted in a nitrogen atmosphere purified from oxygen with the help of an ethereal solution of triphenylmethylsodium.

Results of measurements are detailed in Table 2.

Determination of ether in the complex compound dilithium-benzophenone-p-tolylimide. 18.5 g benzophenone-p-tolylimide, 1.3 g lithium and 180 ml anhydrous ether were placed in a two-branch ampoule previously filled with dry nitrogen. The reaction mass was shaken for 50 hours. The metal organic compound in the form of a dark-red precipitate was filtered in an atmosphere of nitrogen and dried for 3 hours in vacuum (2 mm). Anhydrous benzene was then poured into the funnel and water was carefully added dropwise. The benzene solution was transferred to a Favorsky flask and fractionated to give 1.2 g ether with b. p. 35-36°.

SUMMARY

1. Dilithium and disodium compounds of azomethines, obtained in an ethereal medium, are complex compounds containing 1 to 2 molecules of combined ether.

2. Etherates of alkali organic compounds of azomethines are electrically conductive.

3. In the etherates of dimetal compounds of azomethines, one atom of metal, coordinatively bound to ether, is in the ionized state, while the second atom of metal is covalently bound to the carbon atom of the azomethine bond.

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REACTION OF THE COMPLEX SALT OF p-NITROPHENYLDIAZONIUM AND FERRIC CHLORIDE WITH ALCOHOLS

A. V. Dombrovsky and M. D. Stadnichuk

Aromatic diazonium salts react with alcohols in two main directions: either the alcohols are oxidized to carbonyl compounds and aromatic hydrocarbons (or their derivatives) are formed [1] or ethers are obtained [2]. The particular direction of the reaction depends on the character of the substituents in the aromatic nucleus of the diazonium, the chemical nature of the alcohol and other factors.

In a study of the action of the complex of p-nitrophenyldiazonium chloride with ferric chloride, we noted that in the reaction with ethyl alcohol the complex is nearly entirely transformed into p-nitrochlorobenzene. Subsequently we tested the action of a series of alcohols on this complex.

Complex compounds of aryldiazonium chlorides with chlorides of a series of metals were first prepared and described by K. A. Kocheshkov and A. N. Nesmeyanov [3]. Of greatest interest are the complex salts of iron since they are easily accessible, convenient for handling, and extremely reactive.

Our experiments showed that the complex salt of ferric chloride with p-nitrophenyldiazonium chloride is decomposed by alcohols with evolution of nitrogen from the diazo group and with formation of p-nitrochlorobenzene, the amount of the latter decreasing (see table) with increasing molecular weight of the alcohol. Since alcohols can be regarded as derivatives of water, we attempted to decompose the complexes with water under similar conditions, and it was found that water slowly decomposes the complex at room temperature. p-Nitrochlorobenzene was isolated from the complex reaction product in the amount of only 11%.

R—OH	Yield of p-nitrochlorobenzene (in %)	By-products	Reaction conditions
H_2O	11	—	Room temperature
CH_3OH	87	Methylal	
C_2H_5OH (anhydrous)	87	Acetaldehyde	
C_2H_5OH (reactive)			
Iso-C_3H_7OH	83	Acetone	Heating to 25-30° followed by cooling
Iso-C_4H_9OH	79	Isobutyraldehyde	
Iso-$C_5H_{11}OH$	70	Isovaleraldehyde	
$C_6H_5CH_2OH$	34	Benzaldehyde	With cooling

In addition to p-nitrochlorobenzene the decomposition of the complex with alcohols gave small amounts of nitrobenzene and the corresponding carbonyl compounds; these were identified. Thus, in the case of ethyl alcohol acetaldehyde is formed; in the reaction with isopropyl alcohol acetone is formed, and so on. In the case, however, of methyl alcohol traces of a substance with a pleasant odor, reminiscent of methylal, are obtained. Formation of carbonyl compounds is evidently due to the oxidizing action of the diazonium salt in the complex.

Decomposition of the complex salt in alcohols is, judging by the results, a reaction similar to the Sandmeyer reaction and evidently proceeds by a free-radical mechanism. Since the complex salt is readily soluble in alcohols, the first step is undoubtedly the formation of solvates. Subsequently, under the influence of the alcohol molecules, the complex, with a structure of the ionic type [4], rearranges to the nonionic diazobenzene chloride, which spontaneously breaks down to free radicals:

$$(ArN_2^+ FeCl_4^-) \cdot xROH \longrightarrow (Ar-N=N-Cl \cdot FeCl_3) \cdot xROH \longrightarrow$$
$$\longrightarrow xROH + N_2 + FeCl_3 + Ar\cdot + Cl\cdot \longrightarrow Ar-Cl,$$

where Ar = $p\text{-}NO_2C_6H_4$.

EXPERIMENTAL

By the method of Kocheshkov and Nesmeyanov [3, 4] 28 g p-nitroaniline (m. p. 146-147°) gave 60 g (76%) complex salt $p\text{-}O_2NC_6H_4N_2Cl \cdot FeCl_3$. M. p. 91-92° (with decomp.).

Reaction of complex with methyl alcohol. To 7 g complex salt was added 10 ml dry methyl alcohol (b. p. 64.5-65°). Nitrogen at once started to come off and 386 ml was collected. In course of reaction the salt dissolved, after 1 1/2 hours the decomposition was finished, and yellow crystals quickly came down. The reaction mixture had a pleasant fruity odor. The crystals were washed with water and dried; m. p. 82-83°. A mixed melting test with a specimen of p-nitrochlorobenzene did not show a depression. Yield 2.75 g. Reduction of the prepared p-nitrochlorobenzene gave p-chloroaniline (m. p. 69°). In the liquid after separation of the crystals of p-nitrochlorobenzene were detected traces of nitrobenzene (organoleptically – from the odor – and by reduction in alcohol with zinc followed by oxidation of the reduction product with potassium permanganate).

The experiments with the remaining alcohols and water were carried out under similar conditions. Data are presented in the table.

SUMMARY

1. The complex salt of p-nitrophenyldiazonium chloride with ferric chloride is decomposed by alcohols with formation of p-nitrochlorobenzene, the maximum yields of which are obtained by the action of the first three members of the homologous series of saturated alcohols.

2. Formation of p-nitrochlorobenzene is accompanied by side reactions, in particular the oxidation of alcohols to carbonyl compounds.

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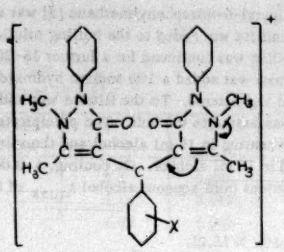
DYES CONTAINING ANTIPYRINE RINGS

V. HYDROLYSIS OF DYES CONTAINING SUBSTITUENTS IN THE ORTHO-POSITION

O. F. Ginzburg and D. V. Ioffe

The hydrolysis constants of dyes containing antipyrine nuclei, with the general formula (I), depend to a considerable extent upon the character and position of the substituent X. It was earlier shown that the introduction into antipyrine dyes of electron-donating substituents in the para-position to the central carbon atom lowers the hydrolysis of the dyes [1]. This is explained by assuming that the migration of an unshared electron pair of the electron-donating substituents to the central carbon atom causes in the latter a fall in the magnitude of the positive change which leads to stabilization of the cation.



(I)

When present in the ortho-position to the carbon atom, electron-donating substituents likewise lower the hydrolysis of dyes. Thus, for example, the hydrolysis constant of dyes (synthesized by us) containing a methoxyl group in the phenyl nucleus in the ortho-position to the central carbon atom is approximately 7 times lower than the hydrolysis constant of the unsubstituted dye known as Antipyrine Orange.

On the other hand the introduction of electron-accepting substituents into antipyrine dyes in the para-position to the central carbon atom intensifies the hydrolysis of the dyes. As we see from the data of Table 1, the nitro group, as was to be expected in view of the difference in the electron-accepting character of the substituents, exerts a stronger effect than the sulfo group, and the latter in turn has a stronger effect than a chlorine atom [2].

TABLE 1

Temperature 17 ± 1°

Number of preparation	X	K_r	
		o	p
1	SO_3H	$2.5 \cdot 10^{-11}$	$2.4 \cdot 10^{-6}$
2	NO_2	$5.6 \cdot 10^{-8}$	$1.8 \cdot 10^{-5}$
3	Cl	$1.4 \cdot 10^{-7}$	$8.0 \cdot 10^{-7}$
4	H	$2.5 \cdot 10^{-7}$	

An entirely different picture was obtained on studying the hydrolysis of antipyrine dyes containing the same electron-accepting substituents but in the ortho-position to the central carbon atom. It was found that all these dyes are more stable to hydrolysis than Antipyrine Orange, the dye possessing a sulfo group (Table 1) having the lowest hydrolysis constant. Thus the electron-accepting action of chlorine and of nitro and sulfo groups in the ortho-position to the central carbon atom has superposed on it a stronger and opposite effect evidently resulting from shielding of the central carbon atom by the above-mentioned substituents.

EXPERIMENTAL

1. Diantipyryl-o-methoxyphenylmethane. (Base.) To a solution of 15.0 g (0.08 mole) antipyrine and 5.45 g (0.04 mole) o-methoxybenzaldehyde in 90 ml alcohol was added 30 ml hydrochloric acid (d 1.17). The next day the white precipitate was filtered and the alcohol was distilled off from the filtrate. A fresh portion of hydrochloride was thus brought down and was filtered and mixed with the first portion of salt. The base was obtained by treating the hydrochloride with 10% sodium hydroxide solution. Yield 13.0 g (66%) of base with m. p. 210°.

After two crystallizations from a 1:1 benzene-gasoline mixture, the m. p. was 216-217°. Further crystallization did not raise the m. p. further.

Found %: N 11.56, 11.55. $C_{30}H_{30}O_3N_4$. Calculated %: N 11.33.

The hydrochloride was crystallized from water and dried to constant weight at 80°. M. p. 184-185° (decomp.). The hydrogen chloride content of the salt was determined by titration of the aqueous acetone solution.

Found %: HCl 6.87. $C_{30}H_{30}O_3N_4 \cdot HCl$. Calculated %: HCl 6.89.

The picrate of the base crystallizes from alcohol with m. p. 165-166°

Found %: N 13.88. $C_{30}H_{30}O_3N_4 \cdot C_6H_3O_7N_3$. Calculated %: N 13.55.

2. Diantipyryl-o-chlorophenylmethane. (Base.) To a solution of 13.2 g (0.07 mole) antipyrine and 4.5 g (0.035 mole) o-chlorobenzaldehyde in 90 ml alcohol was added 30 ml hydrochloric acid (d 1.17). The following day the alcohol was distilled off from the solution, twice the amount of water was added and the mass was cooled. The white precipitate was filtered and washed on the filter with water until the acid reaction to congo had disappeared. Yield 12.2 g (70%) product with m. p. 256-258°. After two crystallizations from a 1:1 mixture of benzene and gasoline the compound melted at 260-261°.

Found %: N 11.48, 11.38. $C_{29}H_{27}O_2N_4Cl$. Calculated %: N 11.25.

The picrate of the base crystallizes from alcohol, m. p. 199-200°.

Found %: N 13.71. $C_{29}H_{27}N_4O_2Cl \cdot C_6H_3O_7N_3$. Calculated %: N 13.47.

3. Picrate of diantipyryl-o-nitrophenylcarbinol. 2.0 g diantipyryl-o-nitrophenylmethane [2] was dissolved with heating in 20 ml hydrochloric acid (d 1.17), and 0.2 g sodium nitrite was added to the boiling solution, followed in the course of 20 minutes by 0.5 ml nitric acid (d 1.4). Boiling was continued for a further 15-20 minutes and the mass was poured into 100 ml cold water. To the reaction mass was added a 10% sodium hydroxide solution until the acid reaction to congo had disappeared; it was then cooled and filtered. To the filtrate was added sodium hydroxide solution until the reaction was strongly alkaline, and it was heated to the boil. The precipitated carbinol was collected. Yield 1.5 g (30%). The carbinol was dissolved with heating in 10 ml alcohol and the solution was filtered; to the filtrate was added a hot solution of 0.8 g picric acid in 10 ml alcohol. On cooling, a dark-red precipitate came down and melted at 130-132° after two crystallizations from aqueous alcohol λ_{max} of the cation of the dye 490 mμ.

Found %: N 15.13, 15.12. $C_{29}H_{26}O_4N_5 \cdot C_6H_2O_7N_3$. Calculated %: N 15.21.

4. Picrate of diantipyryl-o-methoxyphenylcarbinol. The preparation was on the same lines as that of the picrate of diantipyryl-o-nitrophenylcarbinol. Crystallizes from aqueous alcohol. M. p. 134-136°. λ_{max} of the cation of the dye 490 mμ.

Found %: N 13.46, 13.68. $C_{30}H_{29}O_3N_4 \cdot C_6H_2O_7N_3$. Calculated %: N 13.59.

5. Picrate of diantipyryl-o-chlorophenylcarbinol. Preparation was on the same lines as for the picrate of diantipyryl-o-nitrophenylcarbinol. Crystallizes from aqueous alcohol. M. p. 109-112°. λ_{max} of the cation of the dye: 495 mμ.

Found %: N 13.87, 13.82. $C_{29}H_{26}O_2N_4Cl \cdot C_6H_2O_7N_3$. Calculated %: N 13.52.

6. Determination of hydrolysis constants of the dyes. $5 \cdot 10^{-5}$ mole of dye picrate was dissolved in 50 ml acetone. To a slightly buffered solution with a volume of 25.0 ml, with a different pH, was added one and the same amount of the above solution. After equilibrium had been established in the solution, the optical density of the latter was measured on a König-Martens spectrophotometer at a wavelength of 490 mμ and with layer thicknesses of the investigated solution as indicated below. The results are set forth in Table 2 which also gives the pK_r of the dyes. The constants were calculated from the formula: $pK_r = pH - \log \frac{1-a}{a}$; $a = \frac{E}{E_{max}}$, where E is the optical density of the solution under examination and E_{max} is the optical density of the solution in which hydrolysis of the dye is substantially completely suppressed.

7. Diantipyryl-p-sulfophenylmethane. To a solution of 3.0 g (0.0145 mole) p-sulfobenzaldehyde (sodium salt) and 5.5 g (0.029 mole) antipyrine in 50 ml water was added 25 ml hydrochloric acid (d 1.17) and the solution was stood overnight. The precipitate was then collected and washed with water until the acid reaction to congo had disappeared. Yield 7.6 g substance (93%).

The product crystallizes from alcohol. Decomp. p. 300-302°.

Found %: S 5.79; N 10.43. M 544.1, 545.3. $C_{29}H_{28}O_5N_4S$. Calculated %: S 5.87; N 10.29. M 544.5.

TABLE 2

Temperature 17 ± 1°

Number of preparation	Name of dye	Solution of dye (in ml)	Thickness of layer (in mm)	pH	E	pK_r
1	Diantipyryl-o-methoxyphenylcarbinol picrate	1.0	20	6.0	0.478	–
				7.12	0.330	7.47
				7.36	0.250	7.43
				7.84	0.150	7.49
2	Diantipyryl-o-nitrophenylcarbinol picrate	1.2	20	6.34	0.353	–
				7.40	0.140	7.23
				7.81	0.080	7.27
3	Diantipyryl-o-chlorophenylcarbinol picrate	0.6	50	5.9	1.060	–
				6.6	0.660	6.9
				7.1	0.370	6.8
				7.6	0.178	6.9

TABLE 3

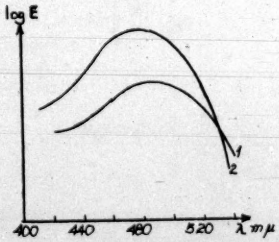
Temperature 17 ± 1°

Number of preparation	pH	E	pK_r
1	3.4	0.863	–
2	5.45	0.563	5.65
3	6.00	0.245	5.60

TABLE 4

Temperature 17 ± 1°

Number of preparation	pH	E	pK_r
1	5.0	1.010	–
2	10.4	0.650	10.6
3	10.7	0.442	10.6



8. Oxidation of diantipyryl-p-sulfophenylmethane to the dye. 3 g diantipyryl-p-sulfophenylmethane was dissolved by heating in 30 ml hydrochloric acid (d 1.17) and addition was made at the boil of 0.3 g sodium nitrite, followed by dropwise addition over a period of half an hour of 1.0 ml nitric acid (d 1.4). Boiling was continued for a further 20-30 minutes (until appearance of a resin on the walls of the flask), and the mixture was poured into a beaker containing 50 ml water. The mixture was cooled and filtered; the filtrate was evaporated to dryness on a water bath. The residue was dissolved in water, filtered and again evaporated to give 1.7 g technical dye, chromatographic analysis of which showed that it did not contain colored impurities.

The synthesized acid dye colors wool an orange color. Reducing agents decolorize solutions of the dye. The absorption spectrum of the dye is shown in curve 1 of the diagram.

0.5 g dye was dissolved in 50 ml water and 3.0 ml of the solution was added to 25 ml buffer solution. The hydrolysis constant of the dye was determined as described above. The thickness of the layer of solution was 50 mm. Results are presented in Table 3.

9. Diantipyryl-o-sulfophenylmethane. The preparation was carried out on the same lines as that of diantipyryl-p-sulfophenylmethane. Yield 73%. Decomp. p. 288-290°.

Found %: N 10.46. M 547.5, 545.0. $C_{29}H_{28}O_5N_4$. Calculated %: N 10.29. M 544.5.

10. Oxidation of diantipyryl-o-sulfophenylmethane to the dye. Oxidation of diantipyryl-o-sulfophenylmethane and isolation of the resultant dye were carried out on the same lines as the preparation of dye from diantipyryl-p-sulfophenylmethane. From 3 g leuco compound was formed 1.9 g technical dye, the chromatographic analysis of which showed that it does not contain colored impurities. The prepared acid dye colors wool orange. Solutions of the dye are decolorized under the action of reducing agents. The absorption spectrum of the dye is represented by curve 2 in the diagram.

0.05 g dye was dissolved in 50 ml water and 1.0 ml of the solution was added to 25 ml buffer solution. The hydrolysis constant of the dye was determined as described above. Thickness of layer 20 mm. Results are set forth in Table 4.

SUMMARY

In a series of antipyrine dyes, substituents in the ortho-position to the central carbon atom enhance the stability of the dyes towards hydrolysis regardless of whether the substituents are electron donators or electron acceptors.

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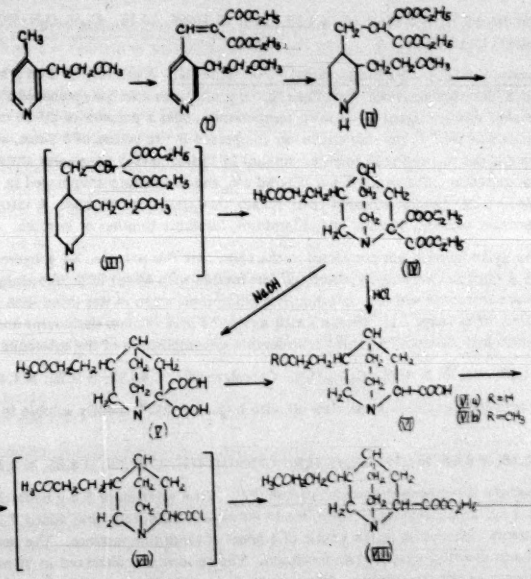
*T. p. = C. B. Translation pagination

SYNTHESIS OF THE ETHYL ESTER OF 5-(β-METHOXYETHYL)-QUINUCLIDINE-2-CARBOXYLIC ACID

M. V. Rubtsov and L. N. Yakhontov

Our previously described synthesis of 5-(β-hydroxyethyl)-quinuclidine-2-carboxylic acid [1] is characterized by a multidirectional course of condensation of 3-(β-acetoxyethyl)-4-methylpyridine with dihydroxymalonic ester due to the presence of a labile acetyl group in the pyridine component. With the aim of avoiding side reactions at this stage and of improving the yield of substituted dicarbethoxyvinyl pyridine, we used 3-(β-methoxyethyl)-4--methylpyridine for condensation with dihydroxymalonic ester [2].

The synthesis of the ethyl ester of 5-(β-methoxyethyl)-quinuclidine-2-carboxylic acid was realized according to the following scheme:



3-(β-Methoxyethyl-4-methylpyridine was condensed with dihydroxymalonic ester to form 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine (I) which was isolated in the form of the hydrochloride in a yield of 58%.

Hydrogenation of (I) in presence of platinum catalyst, prepared by Adams' method, proceeds at a variable rate, slowing down markedly after absorption of the hydrogen going into the hydrogenation of the vinyl group. The final product of hydrogenation – 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine (II) – readily reacts with bromine in chloroform solution at room temperature to form the bromo derivative (III), which on boiling with pyridine undergoes cyclization to 5-(β-methoxyethyl)-2,2-dicarbethoxyquinuclidine (IV).

On boiling 5-(β-methoxyethyl)-2,2-dicarbethoxyquinuclidine with concentrated hydrochloric acid, saponification takes place followed by decarboxylation of the resultant dicarboxylic acid. Simultaneously the methoxyl group undergoes hydrolysis so that the final product is 5-(β-hydroxyethyl)-quinuclidine-2-carboxylic acid (VIa). The methoxyl group remains intact on alkaline saponification of 5-(β-methoxyethyl)-2,2-dicarbethoxyquinuclidine. The resultant 5-(β-methoxyethyl)-quinuclidine-2,2-dicarboxylic acid (V) readily decarboxylates when heated in vacuum to 160°. Treatment of 5-(β-methoxyethyl)-quinuclidine-2-carboxylic acid (VIb) with thionyl chloride gives the acid chloride (VII) treatment of which with anhydrous alcohol leads to formation of the ethyl ester of 5-(β-methoxyethyl)-quinuclidine-2-carboxylic acid (VIII).

EXPERIMENTAL

3-(β-Methoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine (I). A mixture of 23.0 g 3-(β-methoxyethyl)-4-methylpyridine, 32.8 g dihydroxymalonic ester and 100 ml acetic anhydride was heated 8 hours on a boiling water bath. The reaction mass was evaporated in a vacuum on a boiling water bath and the residue distilled in vacuum (0.3 mm) to give 35.0 g viscous, light-yellow oil boiling at 145-160°. The base obtained was dissolved in anhydrous ether and the solution treated with the theoretical amount of alcoholic solution of hydrogen chloride to give the hydrochloride of 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine. The latter was filtered and twice recrystallized from anhydrous toluene. The second recrystallization gave 30.6 g hydrochloride with m. p. 98.5-99°. Yield 58.5% reckoned on the 3-(β-methoxyethyl)-4-methylpyridine taken into the reaction. The hydrochloride of 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine forms lustrous, colorless, hexagonal plates, very easily soluble in water, acetone, alcohol, benzene and hot toluene, poorly soluble in cold toluene, insoluble in ether.

Found %: C 55.98, 55.70; H 6.43, 6.80; N 3.97, 3.98; Cl 10.26, 10.16. $C_{16}H_{21}O_5N \cdot HCl$. Calculated %: C 55.89; H 6.44; N 4.07; Cl 10.33.

3-(β-Methoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine (II). A mixture of 23.4 g hydrochloride of 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine (I), 0.6 g platinum catalyst (prepared by Adams' method) and 100 ml anhydrous alcohol was hydrogenated at room temperature under a pressure of 20-30 cm water column. Hydrogenation of the double bond in the side chain was completed in the course of 5 hours, after which the reaction slowed down abruptly and the theoretically required amount of hydrogen (6.1 liters) was absorbed only after 12 days from the start of hydrogenation. The catalyst was filtered off, and the filtrate evaporated in vacuum to give 23.85 g hydrochloride of 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine. A viscous, syrupy oil, soluble in water, alcohol, benzene, toluene, acetone and chloroform, insoluble in ether or ligroine. Quantitative yield.

A portion of the hydrochloride was converted to the base. For this purpose, 3.5 g hydrochloride of 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine was treated with 30 ml 50% potassium carbonate solution, and the resultant oil was extracted with chloroform. The chloroform solution was dried with potassium carbonate and the solvent distilled off to leave 30 g residue which was dried in a vacuum desiccator and analyzed without distillation since even in high vacuum (0.2 mm) considerable decomposition of the substance occurs.

Found %: C 61.26; H 8.70; N 4.25. $C_{16}H_{29}O_5N$. Calculated %: C 60.96; H 9.20; N 4.44.

The N-acetyl derivative of (II) is a colorless oil with b. p. 215-217°, readily soluble in organic solvents, insoluble in water.

Found %: C 60.56; H 8.55; N 4.16. $C_{18}H_{31}O_6N$. Calculated %: C 60.50; H 8.68; N 3.92.

5-(β-Methoxyethyl)-2,2-dicarbethoxyquinuclidine (IV). To a solution of 8.4 g hydrochloride of 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine in 80 ml dry chloroform was added a solution of 3.9 g bromine in 50 ml chloroform with stirring in the course of 5 hours at room temperature. The resultant solution was stirred for another 8 hours and then evaporated in vacuum. The residue was dissolved in 20 ml water and treated with 20 ml 50% potassium carbonate solution. The separated oil was extracted with ether, the ether was removed, and the 3-(β-methoxyethyl)-4-(β,β-dicarbethoxy-β-bromoethyl)-piperidine was cyclized by boiling with 50 ml dry pyridine for 2 hours. The pyridine was distilled off and the hydrobromide of 5-(β-methoxyethyl)-2,2-dicarbethoxyquinuclidine, remaining in the form of a thick, dark oil, was converted to the base by treatment with 50% potassium carbonate solution. The base was extracted with ether, the ether was distilled off, and the base distilled in vacuum (0.4 mm). The fraction coming over at 132-170° was collected.

There was obtained 5.5 g (74.7%) 5-(β-methoxyethyl)-2,2-dicarbethoxyquinuclidine. A light-yellow oil, readily soluble in organic solvents, poorly soluble in water.

On boiling 5-(β-methoxyethyl)-2,2-dicarbethoxyquinuclidine with concentrated hydrochloric acid, saponification takes place followed by decarboxylation of the resultant dicarboxylic acid. Simultaneously the methoxyl group undergoes hydrolysis so that the final product is 5-(β-hydroxyethyl)-quinuclidine-2-carboxylic acid (VIa). The methoxyl group remains intact on alkaline saponification of 5-(β-methoxyethyl)-2,2-dicarbethoxyquinuclidine. The resultant 5-(β-methoxyethyl)-quinuclidine-2,2-dicarboxylic acid (V) readily decarboxylates when heated in vacuum to 160°. Treatment of 5-(β-methoxyethyl)-quinuclidine-2-carboxylic acid (VIb) with thionyl chloride gives the acid chloride (VII) treatment of which with anhydrous alcohol leads to formation of the ethyl ester of 5-(β-methoxyethyl)-quinuclidine-2-carboxylic acid (VIII).

EXPERIMENTAL

3-(β-Methoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine (I). A mixture of 23.0 g 3-(β-methoxyethyl)-4-methylpyridine, 32.8 g dihydroxymalonic ester and 100 ml acetic anhydride was heated 8 hours on a boiling water bath. The reaction mass was evaporated in a vacuum on a boiling water bath and the residue distilled in vacuum (0.3 mm) to give 35.0 g viscous, light-yellow oil boiling at 145-160°. The base obtained was dissolved in anhydrous ether and the solution treated with the theoretical amount of alcoholic solution of hydrogen chloride to give the hydrochloride of 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine. The latter was filtered and twice recrystallized from anhydrous toluene. The second recrystallization gave 30.6 g hydrochloride with m. p. 98.5-99°. Yield 58.5% reckoned on the 3-(β-methoxyethyl)-4-methylpyridine taken into the reaction. The hydrochloride of 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine forms lustrous, colorless, hexagonal plates, very easily soluble in water, acetone, alcohol, benzene and hot toluene, poorly soluble in cold toluene, insoluble in ether.

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A portion of the hydrochloride was converted to the base. For this purpose, 3.5 g hydrochloride of 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine was treated with 30 ml 50% potassium carbonate solution, and the resultant oil was extracted with chloroform. The chloroform solution was dried with potassium carbonate and the solvent distilled off to leave 30 g residue which was dried in a vacuum desiccator and analyzed without distillation since even in high vacuum (0.2 mm) considerable decomposition of the substance occurs.

Found %: C 61.26; H 8.70; N 4.25. $C_{16}H_{29}O_5N$. Calculated %: C 60.96; H 9.20; N 4.44.

The N-acetyl derivative of (II) is a colorless oil with b. p. 215-217°, readily soluble in organic solvents, insoluble in water.

Found %: C 60.56; H 8.55; N 4.16. $C_{18}H_{31}O_6N$. Calculated %: C 60.50; H 8.68; N 3.92.

5-(β-Methoxyethyl)-2,2-dicarbethoxyquinuclidine (IV). To a solution of 8.4 g hydrochloride of 3-(β-methoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine in 80 ml dry chloroform was added a solution of 3.9 g bromine in 50 ml chloroform with stirring in the course of 5 hours at room temperature. The resultant solution was stirred for another 8 hours and then evaporated in vacuum. The residue was dissolved in 20 ml water and treated with 20 ml 50% potassium carbonate solution. The separated oil was extracted with ether, the ether was removed, and the 3-(β-methoxyethyl)-4-(β,β-dicarbethoxy-β-bromoethyl)-piperidine was cyclized by boiling with 50 ml dry pyridine for 2 hours. The pyridine was distilled off and the hydrobromide of 5-(β-methoxyethyl)-2,2-dicarbethoxyquinuclidine, remaining in the form of a thick, dark oil, was converted to the base by treatment with 50% potassium carbonate solution. The base was extracted with ether, the ether was distilled off, and the base distilled in vacuum (0.4 mm). The fraction coming over at 132-170° was collected.

There was obtained 5.5 g (74.7%) 5-(β-methoxyethyl)-2,2-dicarbethoxyquinuclidine. A light-yellow oil, readily soluble in organic solvents, poorly soluble in water.

n_D^{20} 1.4809, d_4^{20} 1.097, MR_D 80.47; calc. 80.58.

Found %: C 61.75, 61.23; H 8.62, 8.53; N 4.58. $C_{16}H_{27}O_5N$. Calculated %: C 61.34; H 8.62; N 4.47.

The hydrochloride, picrate, methiodide and methylmethosulfate of the diester were isolated in the form of non-crystallizing oils.

5-(β-Hydroxyethyl)-quinuclidine-2-carboxylic acid (VIa) from 5-(β-methoxyethyl)-2,2-dicarbethoxy-quinuclidine. 1.8 g 5-(β-methoxyethyl)-2,2-dicarbethoxyquinuclidine and 20 ml concentrated hydrochloric acid were boiled for 16 hours. After decolorization with charcoal, the solution was evaporated to dryness in vacuum to give 1.3 g (96.3%) hydrochloride of 5-(β-hydroxyethyl)-quinuclidien-2-carboxylic acid in the form of a white amorphous powder.

The acid was identified by esterification. 1.3 g hydrochloride of 5-(β-hydroxyethyl)-quinuclidine-2-carboxylic acid was boiled 6 hours with 12 ml 11% alcoholic solution of hydrogen chloride. The alcohol was distilled off, the residue again dissolved in 12 ml 11% alcoholic solution of hydrogen chloride, and heating continued for a further 6 hours. The solution was evaporated to dryness in vacuum and the residue of hydrochloride of ethyl ester of 5-(β-hydroxyethyl)-quinuclidine-2-carboxylic acid was treated with 20 ml 50% potassium carbonate solution. The base was extracted with ether and the ethereal solution dried with potassium carbonate. The residue after removal of the ether was an oil which was distilled in vacuum. B. p. 102-115° (0.26 mm). Yield 0.13 g (10%) ethyl ester of 5-(β-hydroxyethyl)-quinuclidine-2-carboxylic acid.

Found %: N 6.27, 6.45. $C_{12}H_{21}O_3N$. Calculated %: N 6.16.

5-(β-Methoxymethyl)-quinuclidine-2,2-dicarboxylic acid (V). 3.13 g 5-(β-methoxyethyl)-2,2-dicarbethoxy-quinuclidine and 10 ml 1 N solution of sodium hydroxide were boiled 22 hours. The reaction mass was extracted with chloroform to remove unsaponified ester, acidified with 10 ml 1 N hydrochloric acid, and evaporated to dryness in vacuum. The dicarboxylic acid was extracted from its mixture with sodium chloride with anhydrous alcohol. Removal of the alcohol in vacuum left 1.9 g (64.5%) 5-(β-methoxyethyl)-quinuclidine-2,2-dicarboxylic acid in the form of a white amorphous powder, readily soluble in water and alcohol, poorly soluble in ether.

The hydrochloride was prepared by adding alcoholic solution of hydrogen chloride to an alcoholic solution of the free acid; it was recrystallized from alcohol. A white crystalline powder, insoluble in ether, benzene and toluene, poorly soluble in alcohol and acetone, readily soluble in chloroform and water. M. p. 182° (decomp.).

Found %: Cl 12.01. $C_{12}H_{19}O_5N \cdot HCl$. Calculated %: Cl 12.09.

5-(β-Methoxyethyl)-quinuclidine-2-carboxylic acid (VIb). 1.0 g 5-(β-methoxyethyl)-quinuclidine-2,2--dicarboxylic acid was heated at 160° (petroleum jelly bath) for 15 minutes at a residual pressure of 10 mm; decarboxylation took place with formation of 0.8 g (98.6%) 5-(β-methoxyethyl)-quinuclidine-2-carboxylic acid in the form of an amorphous white powder, insoluble in ether, readily soluble in water, alcohol, acetone, chloroform and benzene.

The hydrochloride is a white crystalline powder with m. p. 190-191° (decomp.), readily soluble in water, alcohol, chloroform and glacial acetic acid, insoluble in ether, acetone and benzene.

Found %: C 52.56; H 7.96; N 5.55; Cl 13.90. $C_{11}H_{19}O_3N \cdot HCl$. Calculated %: C 52.90; H 8.01; N 5.61; Cl 14.23.

Ethyl ester of 5-(β-methoxyethyl)-quinuclidine-2-carboxylic acid (VIII). A mixture of 0.5 g 5-(β--methoxyethyl)-quinuclidine-2-carboxylic acid and 10 ml thionyl chloride was heated 4 hours at 60° (water bath). The solution was evaporated in a vacuum and the residual thionyl chloride removed by double addition of anhydrous benzene followed by vacuum distillation. The hydrochloride of 5-(β-methoxyethyl)-quinuclidine-2--carboxylic acid chloride was heated at the boil with 10 ml anhydrous alcohol for 5 hours. The solution was then evaporated in vacuum; the residue was treated with 10 ml 50% potassium carbonate solution and the separated base was extracted with ether. The ethereal solution was dried with potassium carbonate, the ether was driven off, and the residual light-yellow oil distilled in vacuum. B. p. 185-195° (0.4 mm). Yield 0.4 g (70%) ethyl ester of 5-(β-methoxyethyl)-quinuclidine-2-carboxylic acid in the form of a colorless liquid, readily soluble in organic solvents, poorly soluble in water.

The hydrochloride, methiodide and chloroplatinate were isolated in the form of non-crystallizing oily substances.

The picrate forms light-yellow crystals with m. p. 152-153°, insoluble in water, ether, alcohol and benzene, soluble in chloroform.

Found %: N 12.08. $C_{12}H_{22}O_3N \cdot C_6H_3N_3O_7$. Calculated %: N 11.91.

SUMMARY

1. The synthesis was realized of 5-(β-methoxyethyl)-quinuclidien-2-carboxylic acid and of its ethyl ester, starting from 3-(β-methoxyethyl)-4-methylpyridine.

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THE INFLUENCE OF THE NATURE OF THE CATALYST UPON THE COURSE OF THE REACTION OF DESTRUCTIVE HALOGENATION OF PHENYLCHLOROSILANES

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We previously observed [1, 2] that one of the characteristics of halogenation (chlorination and bromination) of phenylchlorosilanes in presence of $AlCl_3$, $FeCl_3$ and $SbCl_3$ as catalysts, is a process of destructive halogenation involving cleavage of the original substance and of the reaction product at the C–Si bond with formation of haloaromatic derivatives not containing silicon. In the present paper we describe the results of investigations of the nature of this secondary reaction using phenylchlorosilanes as the starting substances for chlorination.

In this reaction the components are, apart from the compound being chlorinated and elementary chlorine, the catalyst and the evolved hydrogen chloride. Each of these components (chlorine, hydrogen chloride, catalyst) can, individually or jointly, lead under specific conditions to cleavage of the Si–C linkage according to one or other of the following schemes:

$$>C-Si< + Cl_2 \longrightarrow >C-Cl + Cl-Si< \quad (1)$$

$$>C-Si< + HCl \longrightarrow >C-H + Cl-Si< \quad (2)$$

$$>C-Si< + MeCl_3 \longrightarrow >C-MeCl_2 + Cl-Si< \quad (3)$$

(where Me = Al, Fe, Sb).

A reaction similar to (1) was previously observed in the case of some aromatic silanes. Thus, Polis reacted bromine with tetraphenylsilane [3] and noted the formation of bromobenzene in consequence of cleavage of tetraphenylsilane at the C–Si bond. Cleavage of the C–Si bond by the action of bromine was likewise observed in attempts to brominate para-bis-triethylphenylsilane in presence of iron as catalyst [4]. An analogous cleavage with bromine (in presence of water) of nitro derivatives of tetraphenylsilane and other compounds was described by Kipping and Cusa [5], and it was successfully applied by us to some chloro and bromo derivatives of phenylchlorosilanes in verification of their structure [1, 2]. Thus, whereas it is definitely established that the C–Si bond in aliphatic organosilicon compounds is not ruptured under the action of elementary halogens [6], this cannot be claimed to be the case for the aromatic silanes in the light of the above literature citations. On the contrary, the data permit us to infer a certain sensitivity of the C–Si bond in these silanes to the action of elementary halogens.

Nevertheless, this postulate is not confirmed by experiment. Contrary to what was observed by Polis [3] we did not observe any reaction when pure bromine was contacted with phenyltrichlorosilane even at 140-150°; neither bromination nor cleavage of the C–Si bond occurred under these conditions.

Similar results were obtained in experiments on the chlorination of diphenyldichlorosilane with gaseous chlorine at 170-180° in the absence of catalysts. Diphenyldichlorosilane, which particularly easily splits off one of its phenyl groups on reaction with chlorine in presence of catalysts ($AlCl_3$, $FeCl_3$ or $SbCl_3$) under relatively mild conditions (30-60°), proved to be completely inert to chlorine at relatively high temperature and did not then undergo either chlorination or cleavage.

It follows from these observations that thermally activated halogens (chlorine or bromine) do not cleave the C–Si bond in aromatic compounds of silicon.

In order to complete the picture, it was of interest to establish the behavior of the C–Si bond in the compounds in question toward chlorine activated by ultraviolet light. Interaction of aliphatic silanes with chlorine under such conditions proceeds normally with formation of chloro derivatives and is not accompanied by the appearance of fission products [7, 8]. The behavior of aromatic silicon compounds, as can be judged by the results of our experiments on chlorination of diphenyldichlorosilane at 70° and with irradiation by a mercury lamp, was

found to be identical with that of aliphatic silanes in one respect, the C—Si bond being inert to photoactivated chlorine; at the same time neither chlorination nor addition of chlorine to the aromatic nucleus was observed.

These data enable us to conclude that the C—Si bonds in aromatic silanes are at least as inert to elementary chlorine and bromine as the C—Si bond in aliphatic compounds of silicon. This conclusion is also supported by the fact that chlorination of diphenyldichlorosilane in presence of iodine at 125° or of phosphorus pentachloride at 140° leads to formation of chloro derivatives of this compound without cleavage of the C—Si bonds of the original or the final products.

Consequently the destructive chlorination observed during the action of chlorine in presence of certain catalysts cannot be explained as the result of direct interaction between elementary halogen and aromatic silane. We therefore made a study of the reaction of hydrogen chloride with phenylchlorosilanes and their chloro derivatives.

The action of anhydrous hydrogen chloride upon aromatic silanes (in a medium of glacial acetic acid), leading to cleavage of the C—Si bond, has already been described [9], from which it follows that such cleavage reactions are only possible with unsubstituted aromatic silanes under comparatively drastic conditions (at the boiling point of glacial acetic acid), and they proceed extremely slowly. We carried out an experimental check of this reaction under the conditions applicable to the chlorination of diphenyldichlorosilane.

On passing dry hydrogen chloride through diphenyldichlorosilane at 100° for 6 hours, the latter does not suffer cleavage at the C—Si bond, as evident from its complete recovery after the reaction. Similar results were obtained on treating tetrachlorodiphenyldichlorosilane with hydrogen chloride under similar conditions.

It follows from these results that diphenyl- and chlorodiphenyldichlorosilanes at 100° are inert to anhydrous hydrogen chloride.

Since one catalyst or another is customarily used in the process of chlorination of phenylchlorosilanes, we studied the reaction of dichlorodiphenyldichlorosilane with hydrogen chloride in presence of antimony trichloride in solution in the ratio of 1 mole silane to 1 mole $SbCl_3$. In this way we hoped to obtain more precise data about the influence of catalysts upon such reactions. It was found that passage of hydrogen chloride through such a solution at 80° even for 6 hours (10 moles) does not modify the composition of the reaction mixture in any way. Consequently neither phenyl nor chlorophenylchlorosilanes are susceptible at 80-100° to cleavage of the C—Si bond by dry hydrogen chloride even in the presence of chlorination catalysts such as antimony trichloride. Therefore, these reactions cannot be the cause of appearance of cleavage products formed during the chlorination of phenylchlorosilanes as a result of secondary processes.

On the contrary, a study of the reaction of phenylchlorosilanes in presence of chlorination catalysts — aluminum chloride [10], iron chloride [11] and antimony chloride [12] — showed that in a number of cases these agents readily enter into reaction with phenylchlorosilanes. Our experimental data permitted us to reach a definite conclusion about the nature of the secondary, so-called destructive chlorination of phenylchlorosilanes.

It was found that this process takes place only in those cases when the catalyst is, in the temperature conditions of the reaction, capable either as such (for example $FeCl_3$, $AlCl_3$) or in the form of a higher chloride formed during chlorination (for example $SbCl_5$) of bringing about the cleavage of C—Si bonds in the original substances or in the final reaction products.

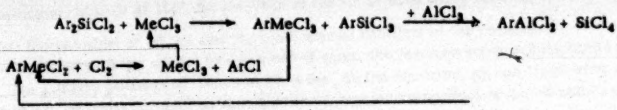
Actually, in the case of chlorination of phenyltrichlorosilane with $SbCl_3$ or $FeCl_3$, neither the original chlorosilane nor its chloro derivatives are susceptible to cleavage at the temperatures employed for chlorination [11, 12], and formation of chlorophenylchlorosilanes is not accompanied by secondary destructive chlorination. However, if the temperature is raised to 140° with the aim of far-reaching chlorination in presence of $FeCl_3$, benzene polychlorides appear among the reaction products. The occurrence under these conditions of a secondary process of cleavage of the products of chlorination of phenyltrichlorosilane is very consistent with the ability of $FeCl_3$ at these temperatures to cleave the polychlorinated derivatives of phenyltrichlorosilane.

In complete analogy, in the case of use of $AlCl_3$ as the catalyst causing cleavage of phenyltrichlorosilane even under ordinary conditions [10], the products of chlorination of phenyltrichlorosilane even at low temperatures always contain considerable amounts of chloro derivatives of benzene which are evidently formed by the cleaving action of the catalyst.

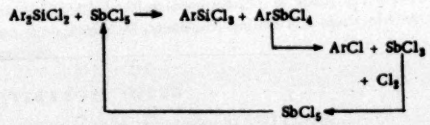
Unlike phenyltrichlorosilane and its chloro derivatives, diphenyldichlorosilane and chlorodiphenyldichlorosilanes are susceptible to cleavage by the action of $FeCl_3$ and $SbCl_5$ with rupture of one of the phenyl radicals [11, 12], while under the action of $AlCl_3$ both radicals are ruptured under relatively mild conditions of temperature [10].

Consequently among the products of reaction of diphenyldichlorosilane with chlorine, depending upon the catalyst used, are the corresponding products of cleavage – $SiCl_4$, $C_6H_5SiCl_3$ and its chloro derivatives, and chlorobenzenes.

In addition, as seen from our earlier investigations [10, 11, 12], the reaction of phenylchlorosilanes and their chloro derivatives with the chlorides of aluminum, iron and antimony proceeds in such a manner that the products of these reactions are, on the one hand, $SiCl_4$ or $C_6H_5SiCl_3$ and its chloro derivatives, and, on the other hand, organic compounds of aluminum, antimony and iron (the latter as intermediate, unstable compounds). Consideration of the results of these investigations decisively shows that the cause of the secondary process of destructive halogenation taking place during chlorination (or bromination) of phenylchlorosilanes in presence of chlorides of aluminum, iron and antimony is the dearylating action of these catalysts. In respect of dearylating activity the catalysts employed may be arranged in the order $AlCl_3 > FeCl_3 > SbCl_5$, and a more or less intensive course of the secondary process is observed accordingly. The secondary process may be represented generally by the following series of equations:



(where Ar is an aromatic radical, Me = Al, Fe), and in the case of antimony catalysts by the scheme:



Consequently the mechanism of destructive chlorination (or bromination) of phenylchlorosilanes involves formation of organometallic compounds due to the cleaving action of the catalysts, and under the action of chlorine (bromine) these compounds are immediately transformed into $MeCl_3$(Br) so that the catalyst is regenerated and brings about further cleavage of the phenylchlorosilanes, while chloro (bromo) derivatives of benzene appear in the reaction products.

EXPERIMENTAL

Action of bromine on $C_6H_5SiCl_3$ in absence of catalysts. 7.0 g phenyltrichlorosilane and 4.7 g bromine were put in a glass tube. The sealed tube was heated 8 hours at 90°, 8 hours at 110° and 8 hours at 140-150°, after which the tube was opened and its constants were fractionally distilled. The bromine was taken off on a water bath and the residue distilled in vacuum to give 5.4 g liquid with b. p. 70-72° at 7 mm and d_4^{20} 1.3214; this was unchanged phenyltrichlorosilane (83 %). No other products of reaction were isolated.

Chlorination of $(C_6H_5)_2SiCl_2$ in absence of catalysts. A dry stream of chlorination was passed at 170-180° for 15 hours through 10 g diphenyldichlorosilane with a speed of 40 ml/min. At the end of the chlorination, no change in weight of the reaction mass was found. Distillation of the product in vacuum gave 8.5 g liquid with b. p. 145-146° at 7 mm and d_4^{20} 1.2341, which was unchanged diphenyldichlorosilane (85% of the original weight).

Chlorination of $(C_6H_5)_2SiCl_2$ under irradiation by a quartz-mercury lamp. A stream of dry chlorine was passed at 70° and a velocity of 40 ml/min. for 2 hours, through 7 g diphenyldichlorosilane in a quartz tube irradiated with a mercury lamp of the PRK-2 type. The weight of the mass after chlorination was unchanged, and vacuum fractionation gave approx. 6.5 g (93.0%) of unchanged diphenyldichlorosilane.

Reaction of $(C_6H_5)_2SiCl_2$ with hydrogen chloride. A stream of dry hydrogen chloride was passed for 6 hours at 100° through 7.5 g diphenyldichlorosilane. 5.5 g hydrogen chloride was passed through. At the end of the treatment no reaction products were detected; 86.2% of the original diphenyldichlorosilane was recovered on distillation.

Reaction of $(C_6H_5Cl_2)_2SiCl_2$ with hydrogen chloride. A current of dry hydrogen chloride was passed at 100° for 6 hours through 3.0 g tetrachlorodiphenyldichlorosilane. 5.8 g hydrogen chloride was passed through. As in the preceding experiment, no reaction products whatever were detected, the main mass of the original silane (88%) being recovered unchanged.

Reaction of $(C_6H_4Cl)_2SiCl_2$ with hydrogen chloride in presence of $SbCl_3$. A current of dry hydrogen chloride was passed at 80° for 6 hours into a mixture of 10 g dichlorodiphenyldichlorosilane and 7.0 g antimony trichloride. 11.3 g hydrogen chloride was passed through. After this operation, no reaction products whatever were detected. 8.9 g (89%) of the dichlorodiphenyldichlorosilane was recovered unchanged.

Reaction of $C_6H_5SiCl_3$, $(C_6H_5)_2SiCl_2$ and their chloro and bromo derivatives with chlorides of aluminum, iron and antimony. These experiments have already been described [10-12].

SUMMARY

1. A study was made of the behavior of phenyltrichlorosilane, diphenyldichlorosilane and their chloro (bromo) derivatives toward the action of elementary chlorine (bromine) in the absence of catalysts. A study was also made of the reaction of these compounds with hydrogen chloride in the presence and absence of catalysts. It was found that phenylchlorosilanes are inert to anhydrous chlorine and bromine at 170-180° and under ultraviolet irradiation, and also to hydrogen chloride at 100°, no cleavage of the C—Si bond being suffered.

2. It was shown that the chlorides of Al, Fe and Sb, when used as catalysts in the chlorination of phenylchlorosilanes, readily enter into reaction with the silanes in a number of cases, the reaction being accompanied by cleavage of the C—Si bonds. The primary products of these reactions are, on the one hand, silicon-containing compounds ($SiCl_4$, $C_6H_5SiCl_3$ and its chloro derivatives), and, on the other hand, organic compounds of Al, Sb and Fe (the latter as unstable intermediate compounds).

3. The mechanism of the process of destructive chlorination (bromination) of phenylchlorosilanes is discussed; it is assumed that the intermediate products are organometallic compounds formed as a result of cleavage of the phenylchlorosilanes under the action of the catalysts.

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UNSYMMETRICAL ORGANIC α-OXIDES

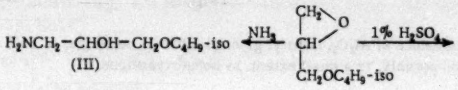
XI. ISOBUTYL GLYCIDYL ETHER AND ITS TRANSFORMATIONS

F. G. Ponomarev, L. N. Cherkasova and R. M. Chernysheva

Ether oxides containing both an oxide and an ether group have not been the subject of many investigations and they present definite interest since syntheses with participation of ether oxides lead to formation of new compounds with mixed functions.

In the present work we studied the reactions of isobutyl glycidyl ether (I) with water, ammonia, diethylamine, methanol and acetone, as well as its isomerization under the influence of alumina.

Under the action of 1% H_2SO_4 isobutyl glycidyl ether (I) adds on water to give a 53% yield of α-monoisobutyl glyceryl ether (II).



(III) (I)

$$\xrightarrow{1\%\ H_2SO_4} CH_2OH-CHOH-CH_2OC_4H_9\text{-iso.}$$

(II)

An attempt to hydrate the ether oxide (I) without a catalyst by heating (100°) gave negative results.

It is interesting that isobutyl glycidyl ether (I) is less resistant to hydration than the previously described isoamyl ether [1] which is substantially not hydrated under the same conditions.

Isobutyl glycidyl ether (I) reacts with ammonia like its homologs [2], but less vigorously, at room temperature to form the 1-isobutyl ether of 3-aminopropane-1,2-diol (III) in 50% yield. The aminoalcohol (III) gives a crystalline picrate. With benzene sulfochloride it forms a benzene sulfo derivative of the composition $C_{19}H_{25}O_5NS_2$.

Formula (III) is accepted for the prepared aminoalcohol on the basis of the Krasusky rule for the order of addition of ammonia to unsymmetrical α-oxides [3].

As was to be expected, ether oxide (I) readily interacts with aqueous diethylamine to give a 61% yield of the 1-isobutyl ether of 3-diethylaminopropane-1,2-diol (IV):

$$CH_3OCH_2CHOH-CH_2OC_4H_9\text{-iso} \xleftarrow{CH_3OH} \text{(I)} \xrightarrow{NH(C_2H_5)_2}$$

(VI)

$$\xrightarrow{NH(C_2H_5)_2} (C_2H_5)_2NCH_2CHOH-CH_2OC_4H_9\text{-iso.}$$

(IV)

The structure of the prepared aminoalcohol (IV) was verified by synthesis from 1-isobutoxy-2-hydroxy-3-chloropropane (V) and diethylamine:

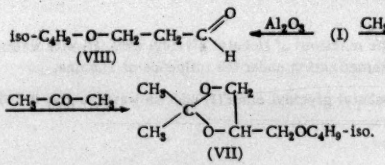
$$\text{iso-}C_4H_9OCH_2CHOHCH_2Cl \xrightarrow{NH(C_2H_5)_2}$$

(V)

$$\xrightarrow{NH(C_2H_5)_2} (C_2H_5)_2NCH_2CHOHCH_2OC_4H_9\text{-iso.}$$

(IV)

With methanol in presence of boron fluoride etherate, the glycidyl ether (I) gives a 55% yield of α, γ-methylisobutyl ether of glycerol (VI). The structure of this α, γ-diether of glycerol (VI) follows from the method of its preparation and is in complete accord with the studies of A. A. Petrov [4] who made a detailed investigation of the order of addition of alcohols to ethers of glycidol. Under the influence of the same catalyst (boron fluoride etherate) the etheroxide (I) reacts in the cold with acetone to form (in 47% yield) 2,2-dimethyl-4-isobutoxymethyldioxolane (VII) whose structure was confirmed by its hydrolysis with 5% H_2SO_4 to the original acetone and α-monoisobutyl glyceryl ether (II).



Under the influence of Al_2O_3, isobutyl glycidyl ether (I) isomerizes at 300° mainly to β-isobutoxy propionaldehyde (VIII) and possibly, to a small extent, to isobutoxyacetone.

EXPERIMENTAL

Isobutyl glycidyl ether (I) was prepared by the same method as for its homologs [5] from the corresponding chloroglyceryl ether and had the constants: b. p. 153-155°, d_4^{20} 0.8980, n_D^{20} 1.4168, in agreement with previous data [6].

Hydration of isobutyl glycidyl ether (I). a) 10 g isobutyl glycidyl ether (I) and 40 ml 1% H_2SO_4 were heated in a sealed tube for 3 hours on a boiling water bath. At the conclusion of the heating, the mixture was extracted several times with ether (50 ml each time), the ethereal extract was dried with potassium carbonate, the ether was distilled off, and the reaction product was distilled in vacuum and then at normal pressure.

B. p. 114-116° at 10 mm and 218-220° at atmospheric pressure, d_4^{20} 1.0025, n_D^{20} 1.4426, MR_D 39.18; calc. 39.22.

Found %: OH 23.86. $C_7H_{16}O_3$. Calculated %: OH 22.97.

The following constants are reported in the literature for this monoether of glycerol, but only for the compound prepared from glycidol [7]: b. p. 216-218°, d^{20} 1.0656.

b) Hydration did not take place on heating a mixture of 5 g ether oxide (I) and 15 ml water on a boiling water bath for 4 hours, and isobutyl glycidyl ether (b. p. 153-156°) was recovered unchanged in the amount of 2.7 g.

Reaction of isobutyl glycidyl ether with ammonia. Condensation of ether oxide (I) with ammonia was effected at room temperature by the usual method [2, 8].

From 13 g (0.1 mole) isobutyl glycidyl ether (I) and 1.30 g 25% aqueous ammonia was obtained, after isolation and purification, 7 g (50%) 1-isobutyl ether of 3-aminopropane-1,2-diol (III).

B. p. 92-93° at 5 mm, d_4^{20} 0.9024, n_D^{20} 1.4439, MR_D 43.00; calc. 41.12.

Found %: N 9.43, 9.90 (Kjeldahl). M 145.6. $C_7H_{17}O_2N$. Calculated %: N 9.52. M 147.2.

The picrate melted at 116-118° (from alcohol).

Found %: N 14.52 (Eckert's method [9]). $C_{13}H_{20}O_9N_4$. Calculated %: N 14.85.

1-Isobutyl ether of 3-aminopropane-1,2-diol (III) is a colorless, mobile liquid with basic properties, readily soluble in water and alcohol, difficultly soluble in ether. Under normal conditions it absorbs CO_2 and H_2O in the air. A sample weighing 0.1592 g increased in weight by 19% after 6 hours. It rapidly decolorizes a chloroform solution of bromine and an aqueous solution of permanganate. It reacts with benzene sulfochloride.

Benzene sulfo derivative of the aminoalcohol (III). To a solution of 0.6 g aminoalcohol (III) in 6 ml pyridine was added 2 ml benzene sulfochloride with shaking. Treatment of the mixture with 15 ml 10% H_2SO_4 brought down the benzenesulfo derivative of aminoalcohol (III) in the form of a yellow oil which crystallized after 24 hours to acicular crystals. After recrystallization from 70% methanol it melted at 90-92°.

Found %: N 3.24 (Kjeldahl). $C_{15}H_{25}O_6NS_2$. Calculated %: N 3.30.

Reaction of isobutyl glycidyl ether with diethylamine. From 13 g (0.1 mole) isobutyl glycidyl ether and 22 g (0.3 mole) diethylamine in 44 ml water was obtained by the usual method [10] 12.5 g (61.5%) 1-isobutyl ether of 3-diethylaminopropane-1,2-diol (IV). In two other similar experiments the yield of (IV) was 62-64%.

B. p. 111-112° at 10 mm, d_4^{20} 0.8881, n_D^{20} 1.4350, MR_D 59.36; calc. 60.11.

Found %: N 6.89 (Kjeldahl); OH 8.70. $C_{11}H_{25}O_2N$. Calculated %: N 7.40; OH 8.37.

A colorless liquid, turning light yellow on keeping. Does not distill at atmospheric pressure without decomposition. Readily soluble in ether and alcohol, poorly soluble in water. Possesses basic properties. Under normal conditions in the air, it absorbs CO_2 and H_2O. A sample of 0.6390 g increased in weight by 1% after 6 hours.

Benzenesulfo derivative of aminoalcohol (IV). To a solution of 0.6 g aminoalcohol (IV) in 6 ml pyridine was added 2 ml benzenesulfochloride with shaking. The product was worked up as above. The benzenesulfo derivative forms colorless crystals with m. p. 75-76°.

Found %: N 3.88. $C_{17}H_{29}O_4NS$. Calculated %: N 4.08.

A crystalline picrate could not be prepared.

For confirmation of the structure of the 1-isobutyl ether of 3-diethylaminopropane-1,2-diol (IV), it was prepared from the α-monoisobutyl ether of glycerol chlorohydrin (i. e. 1-isobutoxy-2-hydroxy-3-chloropropane) (V) and diethylamine.

Condensation of 1-isobutoxy-2-hydroxy-3-chloropropane with diethylamine. A mixture of 4 g (V) (b. p. 96-98° at 15 mm, n_D^{20} 1.4428) and 5.2 g diethylamine was heated 3 hours in a sealed tube on a boiling water bath. The product was then treated with 8 ml water, the upper layer was separated and the lower layer was saturated with solid KOH. The resultant small layer of product was added to the main product which was dried with KOH and fractionated in vacuum to give 2.4 g (49%) 1-isobutyl ether of 3-diethylaminopropane-1,2-diol (IV).

B. p. 108-109° at 10 mm, d_4^{20} 0.8869, n_D^{20} 1.4362, MR_D 60.14; calc. 60.11.

Found %: N 7.55 (Kjeldahl). $C_{11}H_{25}O_2N$. Calculated %: N 6.89.

Benzenesulfo derivative of the aminoalcohol (IV). Preparation was similar to that described in the preceding experiment. It melted at 75-76° and did not give a depression with the above-described benzenesulfo derivative of aminoalcohol (IV) prepared from (I) and diethylamine.

Found %: N 4.38. $C_{17}H_{29}O_4NS$. Calculated %: N 4.08.

Reaction of isobutyl glycidyl ether with methanol. To 4.5 g anhydrous methanol (6-fold excess) was added one drop boron fluoride etherate and 3 g isobutyl glycidyl ether (I); the resultant solution was left in a freezing mixture (−10°) for 2 hours. The excess of the alcohol was then distilled off on a water bath, and the product distilled in vacuum to give 2 g (55%) of the α, γ-diether of glycerol (VI).

B. p. 100-103° at 25 mm, d_4^{20} 0.9414, n_D^{20} 1.4235, MR_D 43.91; calc. 43.95.

Found %: OH 11.47. M 167.2. $C_8H_{18}O_3$. Calculated %: OH 10.58. M 162.11.

A colorless liquid with a pleasant odor. Readily dissolves in alcohol, ether and benzene. Reacts with metallic sodium.

Reaction of isobutyl glycidyl ether with acetone. To a mixture of 55 g acetone and 0.4 ml $BF_3 \cdot O(C_2H_5)_2$ was added in small portions 11 g isobutyl glycidyl ether (I). The temperature of the mixture rose from 21° to 23°.

After standing 24 hours at room temperature, the mixture was washed with saturated potassium carbonate solution (20 ml), and dried with potassium carbonate. The acetone was distilled off and the product distilled first in vacuum and then at normal pressure. Yield 7.6 g (47.5%) 2,2-dimethyl-4-isobutoxymethyldioxolane (VII).

B. p. 127-129° at 67 mm and 192-194° at atmospheric pressure, d_4^{20} 0.9285, n_D^{20} 1.4180, MR_D 51.05; calc. 51.11.

Found : M 184.9. $C_{10}H_{20}O_3$. Calculated : M 188.2.

A colorless liquid with a pleasant odor. Dissolves readily in alcohol and ether, with difficulty in water. Under the action of 5% H_2SO_4 it saponifies even in the cold with formation of acetone and glyceryl monoether (II).

Hydrolysis of the dioxolane (VII). 5.4 g (0.04 mole) of (VII) was shaken with 8 ml 5% H_2SO_4 for 30 minutes. The acetone was then distilled off from the mixture.

From the residue, by salting-out with potassium carbonate and extraction with ether, was separated 2 g (47.7%) α-monoisobutyl glyceryl ether (II).

B. p. 115-117° at 10 mm, d_4^{20} 1.0072, n_D^{20} 1.4364, MR_D 39.51; calc. 39.22.

Found %: OH 22.35. $C_7H_{16}O_3$. Calculated %: OH 22.95.

This substance thus does not differ from that described above and obtained by hydrolysis of the isobutyl ether with 1% H_2SO_4.

The yield of acetone, dried over K_2CO_3, with b. p. 56° was 1.2 g (40%). The acetone gives the iodoform reaction and forms a compound with basic mercury sulfate [11].

Isomerization of isobutyl glycidyl ether (I). From 10 g ether oxide (I) under the action of Al_2O_3 at 300° under conditions similar to those described elsewhere [8], 6.5 g (65%) isomerizate was obtained in the form of a colored liquid with a pungent odor, distilling to the extent of 80% in the range of 60-90°, readily soluble in alcohol and ether, difficultly soluble in water. On distillation of the isomerizate over solid KOH, about 60% of the substance polymerized. With fuchsinesulfurous acid the isomerizate gives a crimson color. It forms a silver mirror with ammoniacal silver oxide solution.

Action of potassium permanganate solution on the isomerizate. To 1 g isomerizate was added 100 ml 1% $KMnO_4$ solution, and the mixture was heated (30 minutes) on a boiling water bath until the pungent odor had disappeared. The manganese dioxide was then filtered off and washed with water. The β-isobutoxypropionic acid formed as a result of oxidation was neutralized with ammonia and isolated as the silver salt.

Found %: Ag 43.00. $C_7H_{13}O_3Ag$. Calculated %: Ag 42.77.

The isomerizate also gives a reaction with sodium nitroprusside. A small amount of isobutoxyacetone is probably also formed as a result of isomerization of the ether oxide (I).

SUMMARY

1. The hydration of isobutyl glycidyl ether (I) under the action of 1% H_2SO_4 was investigated. This ether (I) was found to be hydrolytically less stable than isoamyl glycidyl ether.

2. The condensation of isobutyl glycidyl ether (I) with ammonia, diethylamine, methanol and acetone was studied. The products of this reaction, not described in the literature, were isolated and characterized: 1-isobutyl ether of 3-aminopropane-1,2-diol (III); 1-isobutyl ether of 3-aminopropane-1,2-diol (IV); α,γ-methylisobutyl ether of glycerol (VI); and 2,2-dimethyl-4-isobutoxymethyldioxolane (VII).

3. It was shown that isobutyl glycidyl ether (I) isomerizes under the action of Al_2O_3 to give mainly β-isobutoxypropionaldehyde (VIII) and apparently also a small amount of isobutoxyacetone.

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ALKYLATION OF THIOPHENOLS WITH AMINES

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We showed previously [1] that heating of thiophenols with solutions of methylamine at temperatures above 200° leads to formation of the corresponding methyl ethers of thiophenols. Further study of the reaction has shown that the yields of phenols are extremely high (82-96%). A study was later made of the action of methylamine upon disulfides; it was found that heating under the same conditions of diphenyl disulfide with 20% methylamine solution likewise gives thioanisole, the formation of which may be explained by assuming that disulfide in a methylamine medium undergoes the same cleavage as in a medium of caustic alkalies and sodium carbonate [2, 3].

$$2ArS-SAr + 2H_2O \longrightarrow 3ArSH + ArSO_2H.$$

The resultant thiophenol is further alkylated by methylamine. The yield of thioanisole is 58%.

Our very recent investigations have shown that under the specified conditions (6 hours and 240°) p-thiocresol is also alkylated by other aliphatic amines (dimethylamine, benzylamine)(Table 1), whereas the reaction does not go with aromatic amines (aniline and dimethylaniline).

TABLE 1

Amine	Reaction product	Yield of thioether (in %)
CH_3NH_2	$p\text{-}CH_3C_6H_4SCH_3$	84
$(CH_3)_2NH$	$p\text{-}CH_3C_6H_4SCH_3$	95
$C_6H_5CH_2NH_2$	$p\text{-}CH_3C_6H_4SCH_2C_6H_5$	46

The following mechanism may be suggested for the alkylation of thiophenols with aliphatic amines. The initially formed salt of thiophenol with the amine dissociates into ions, for example, according to the scheme:

$$ArSH + CH_3NH_2 \rightleftharpoons ArS^- + CH_3 \cdot NH_3^+.$$

Since the nitrogen of the ammonium ion carries a whole positive charge, a partial positive charge is formed at the carbon atom due to the inductive effect: $H_3\overset{+\delta}{C} \rightarrow \overset{+}{N}H_3$. Subsequently the reaction goes according to the scheme:

$$ArS^- + \overset{+\delta}{C}H_3 \rightarrow \overset{+}{N}H_3 \rightleftharpoons [ArS^- \ldots\ldots \overset{+\delta}{C}H_3 \cdot \overset{+}{N}H_3] \rightarrow ArSCH_3 + NH_3.$$

This explanation is confirmed by the values of $K_{dis.}$ of the amines, which, for aromatic amines, are considerably smaller than for aliphatic amines (approximately by a factor of 10^5).

TABLE 2

Expt. No.	Starting substance	Duration of heating at 240° (in hours	Reaction product			Oxidation product	
			Formula	Yield (in %)	n_D^{20}	Formula	Melting point
1	C_6H_5SH	6	$C_6H_5SCH_3$	96	1.5869	$C_6H_5SO_2CH_3$	87-87.5°
2	$p\text{-}CH_3C_6H_4SH$	6	$p\text{-}CH_3C_6H_4SCH_3$	84	1.5756 *	$p\text{-}CH_3C_6H_4SO_2CH_3$	88
3	$p\text{-}CH_3C_6H_4SH$	2	$p\text{-}CH_3C_6H_4SCH_3$	82			
4	$p\text{-}ClC_6H_4SH$	6	$p\text{-}ClC_6H_4SCH_3$	87	1.5960	$p\text{-}ClC_6H_4SO_2CH_3$	94-95

* n_D^{16} is given.

EXPERIMENTAL

1) Thiophenol was heated in a sealed tube with 20% aqueous methylamine solution. The reaction mass, consisting of a solution of methylamine below a layer of light-yellowish oil, was separated in a separating funnel.

The lower oily layer was distilled. For the purpose of identification the prepared thioether was oxidized with hydrogen peroxide in acetic acid [4] to the corresponding sulfone. Reaction conditions and results are set forth in Table 2.

2) 4.3 g diphenyl disulfide was heated 6 hours at 240° in a sealed tube with 45 ml 20% methylamine. The brown oil formed during the reaction was separated and distilled at 188-190°. Yield 2.8 g (69%) thioanisole, n_D^{20} 1.5868.

Oxidation of 0.8 g of the prepared thioanisole with hydrogen peroxide in glacial acetic acid gave 0.85 g methylphenyl sulfone, m. p. 86-87°. A mixed test with methylphenyl sulfone (m. p. 87-87.5°) did not give a depression.

3) 2 g p-thiocresol and 16 ml 5 N dimethylamine solution were heated in a sealed tube for 6 hours at 240°. From the reaction mixture was isolated 2.1 g (95%) methyl-p-tolyl sulfide with b. p. 208-211°, n_D^{18} 1.5751. The derived methyl-p-tolyl sulfone melts at 86-87°. A mixed sample with methyl-p-tolyl sulfone did not give a depression of meting point.

4) From the reaction mixture, obtained by heating 2.1 g p-thiocresol for 6 hours at 240° with 4.9 g benzylamine and 5 ml water cooled with ice-salt, was separated 1.65 g (46%) p-tolylbenzyl sulfide with m. p. 35-39.5°. After recrystallization from ligroine, the m. p. was 40-41°. The literature [5] gives 44°.

Oxidation of p-tolylbenzyl sulfide with hydrogen peroxide in acetic acid gave p-tolylbenzyl sulfone, m. p. 144-144.5°. The literature [6] gives m. p. 144-145°.

Found %: C 68.46, 68.59; H 5.91, 5.74. $C_{14}H_{14}O_2S$. Calculated %: C 68.26; H 6.73.

5) 2.1 g p-thiocresol, 6 g dimethyl aniline and 5 ml water were heated in a sealed tube for 6 hours at 240°. Alkali extraction of the dimethylaniline layer gave 1.9 g (90%) of the original p-thiocresol, m. p. 42-43°.

6) 1.3 g p-thiocresol, 5.85 g aniline and 6 ml water were heated in a sealed tube for 6 hours at 240°. Alkali extraction gave 1.25 g (96%) of the original p-thiocresol with m. p. 39-40°.

SUMMARY

It was shown that aromatic mercapto compounds are alkylated in good yields by aliphatic amines at 240°. Aromatic amines do not react with mercapto compounds. Diphenyl disulfide gives thioanisole when heated with aqueous methylamine solution.

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A NEW METHOD OF SYNTHESIS OF ESTERS OF PHOSPHINIC AND THIOPHOSPHINIC ACIDS

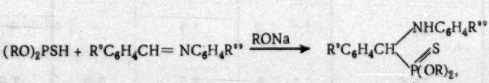
XXI. ADDITION OF DIALKYLTHIOPHOSPHOROUS AND DIALKYLDITHIOPHOSPHOROUS ACIDS TO ANILS

A. N. Pudovik and M. K. Sergeeva

In previous publications, one of us showed that partial esters of phosphorous, thiophosphorous and alkyl- and arylphosphinous acids, as well as esters and nitrile of phosphonacetic acid, phosphonacetone and their homologs possess a nucleophilic character and in presence of alkali metal alkoxides readily add on to unsaturated compounds with formation of various derivatives of esters of phosphinic and thiophosphinic acids [1]. A number of authors recently showed that partial esters of dithiophosphoric acid also possess the ability to combine with unsaturated compounds. Norman, LeSuer and Mastin [2] accomplished the addition of dialkyldithiophosphoric acids to unsaturated hydrocarbons (1-octene , 2-octene and cyclohexene) and to methyl methacrylate. Melnikov and Shvetsova-Shilovskaya [3] added on, apart from unsaturated hydrocarbons, dialkyldithiophosphoric acids to esters and nitriles of unsaturated acids, to unsaturated alcohols and their esters and to unsaturated aldehydes and ketones. Addition of dialkyldithiophosphoric acids to unsaturated organosilicon compounds was accomplished by A. D. Petrov, Mironov and Glukhovtsev [4]. In all these studies mixed esters of dithiophosphoric acids were obtained. Some of them have a fairly strong effect upon insects and may find application as insecticides.

We have developed an extremely simple and convenient method of synthesis of esters of N-substituted aminophosphinic acids consisting in addition of dialkylphosphorous acids and partial esters of ethyl- and phenylphosphinic acids to anils [1]. We have now extended these researches by a study of the additions to various anils of esters of dialkylthiophosphorous and dialkyldithiophosphoric acids.

The reaction between dialkylthiosphosphorous acids and anils was carried out by our previously developed method in presence of alkali metal alkoxides. The course of the reaction may be represented by the following scheme:

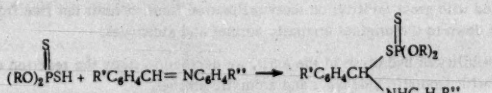


where R = C_2H_5, n-C_4H_9; R' = H, m- and p-CH_3, p-Cl, p-$N(CH_3)_2$; R'' = H, p-OCH_3, m- and p-CH_3.

Table 1 contains the melting points of the products – esters of various derivatives of phenyl-phenylaminomethylthiophosphinic acids – and the results of analyses for phosphorus and sulfur contents; yields are also given.

All the prepared products are crystalline, with a white color, readily soluble in hot alcohol and ether, insoluble in water.

Addition to anils of dialkyldithiophosphoric acids could, thanks to their considerably greater reactivity, be effected in the majority of cases also in the absence of a catalyst when the reaction was conducted in ethyl alcohol solution. The reactions went very easily and were accompanied by heating up of the reaction mixture. Yields of addition products ranged from 80 to 95%. The course of the reaction may be represented by the following equation:



where R = CH_3, C_2H_5; R' = H, p-$(CH_3)_2N$, p-$CH(CH_3)_2$, p-CH_3; R'' = H, p-CH_3, m-CH_3, o-CH_3, p-OCH_3.

The characteristics of the prepared full mixed esters of dithiophosphoric acid are set forth in Table 2.

Addition of dimethyldithiophosphoric acid to p-dimethylaminobenzalaniline was effected in presence of sodium methoxide. The prepared products are yellow crystalline substances, soluble in alcohol, ether, gasoline, dioxane and toluene, partly soluble in hot water.

TABLE 1

Formula	Melting point	Phosphorus (in %)		Sulfur (in %)		Yield (in %)
		Found	Calculated	Found	Calculated	
$C_6H_5CHNHC_6H_4OCH_3$-p | $S{=}P(OC_2H_5)_2$	48°	8.4, 8.3	8.5	9.0	8.8	43.2
p-$(CH_3)_2NC_6H_4CHNHC_6H_5$ | $S{=}P(OC_2H_5)_2$	100-100.5	8.5, 8.0	8.2	8.7	8.5	60.0
$C_6H_5CHNHC_6H_4CH_3$-p | $S{=}P(OC_2H_5)_2$	67	8.8, 8.8	8.9	9.4	9.2	62.3
$C_6H_5CHNHC_6H_4CH_3$-m | $S{=}P(OC_2H_5)_2$	77-78	8.9, 9.2	8.9	9.0	9.2	52.2
m-$CH_3C_6H_4CHNHC_6H_4CH_3$-m | $S{=}P(OC_2H_5)_2$	84-85	8.6, 8.8	8.6	9.1	8.8	50.0
$C_6H_5CHNHC_{10}H_7$ | $S{=}P(OC_2H_5)_2$	136.5	8.2, 8.3	8.0	8.5	8.2	54.1
$C_6H_5CHNHC_6H_5$ | $S{=}P(OC_4H_9)_2$	53	8.0, 8.3	7.9	8.2, 8.4	8.2	78.3
$C_6H_5CHNHC_6H_4OCH_3$-p | $S{=}P(OC_4H_9)_2$	45-46	7.0, 7.3	7.4	–	–	63.2
p-$(CH_3)_2NC_6H_4CHNHC_6H_5$ | $S{=}P(OC_4H_9)_2$	80	6.9, 7.2	7.1	–	–	81.2
m-$CH_3C_6H_4CHNHC_6H_4CH_3$-m | $S{=}P(OC_4H_9)_2$	57-58	7.2, 7.3	7.4	–	–	73.0
p-$CH_3C_6H_4CHNHC_6H_5$ | $S{=}P(OC_4H_9)_2$	36	7.7, 7.9	7.7	–	–	61.3
$C_6H_5CHNHC_6H_4CH_3$-p | $S{=}P(OC_4H_9)_2$	75.5	7.7, 7.8	7.7	7.9	7.9	71.8
$C_6H_5CHNHC_6H_4CH_3$-m | $S{=}P(OC_4H_9)_2$	47-47.5	7.9, 7.8	7.7	7.7, 8.9	7.9	65.6

However, in the case of benzal-p-chloroaniline and p-methylbenzal-dichloroaniline under the usual experimental conditions, we did not succeed in obtaining mixed esters of dithiophosphoric acid. When the reaction mixtures were stood in open dishes in the air, substances with constant melting point crystallized from them; these substances, however, had a very much higher phosphorus constant than was theoretically calculated for the full mixed esters of dithiophosphoric acid.

B. A. Porai-Koshits and A. L. Remizov [5] showed that the anils prepared from weakly basic amines and aromatic aldehydes are hydrolyzed with great facility; on recrystallization from solvents not free from water, or on keeping in the air, they break down to the original aromatic amines and aldehydes.

Bearing in mind the possibility of hydrolysis of the anils, we decided to study the reaction of diethyldithiophosphoric acid directly both with aromatic aldehydes and aromatic amines.

As was shown by Abramov [6], dialkylphosphorous acids in presence of sodium ethoxide readily add on to aliphatic and aromatic aldehydes with formation of esters of hydroxyphosphinic acids. Pudovik and Kitaev [7], in

a study of the reaction between dialkylphosphorous acids and unsaturated aldehydes, showed that the addition takes place at the double bond, as in the case of unsaturated ketones, but at the carbonyl group with formation of unsaturated esters of hydrophosphinic acids. Pudovik and Zametaeva [8] also showed that dialkylthiophosphorous acids behave like dialkylphosphorous acids in the reaction with saturated and unsaturated aldehydes, with formation of esters of unsaturated and saturated hydroxythiophosphinic acids respectively.

TABLE 2

Formula	Melting point	Yield (in %)	Analysis for phosphorus (in %)	
			Found	Calculated
$(C_2H_5O)_2P(=S)-S-CH(C_6H_5)NHC_6H_5$	103-104°	89.1	8.7, 8.4	8.5
$(C_2H_5O)_2P(=S)-S-CH(C_6H_5)NHC_6H_4CH_3$-p	101-102	60.4	8.4, 8.5	8.1
$(C_2H_5O)_2P(=S)-S-CH(C_6H_4N(CH_3)_2\text{-p})NHC_6H_4CH_3$-p	128-130	93.5	8.0, 7.4	7.6
$(C_2H_5O)_2P(=S)-S-CH(C_6H_4N(CH_3)_2\text{-p})NHC_6H_4CH_3$-p	145	95.1	6.9, 7.1	7.6
$(C_2H_5O)_2P(=S)-S-CH(C_6H_4CH(CH_3)_2\text{-p})NHC_6H_4CH_3$-p	109-110	84.1	6.9, 7.1	7.0
$(C_2H_5O)_2P(=S)-S-CH(C_6H_4CH(CH_3)_2\text{-p})NHC_6H_4OCH_3$-p	110-111	57.6	6.8, 6.7	6.9
$(C_2H_5O)_2P(=S)-S-CH(C_6H_4CH_3\text{-p})NHC_6H_4OCH_3$-p	127-128	86.5	7.8, 7.8	7.8
$(CH_3O)_2P(=S)-S-CH(C_6H_4N(CH_3)_2\text{-p})NHC_6H_5$	127	28.9	7.9, 7.8	7.8

Slight heat is developed on carrying out the reaction between diethyldithiophosphoric acid and benzaldehyde, p-tolualdehyde and p-isopropyl benzaldehyde; this exothermic effect is considerably intensified when a few drops of sodium methoxide are introduced into the reaction mixture.

We succeeded in isolating in crystalline form only the product of addition of diethyldithiophosphoric acid to benzaldehyde. Its analysis corresponded to the ester of hydroxybenzyl-diethyldithiophosphoric acid. The reaction apparently goes according to the equation:

$$(C_2H_5O)_2P(=S)-SH + OHCC_6H_5 \longrightarrow (C_2H_5O)_2P(=S)-S-CH(OH)C_6H_5.$$

In respect to constants and composition the hydroxybenzyl-diethyldithiophosphoric ester synthesized in this manner was not identical with the product of reaction of diethyldithiophosphoric acid with benzal-p-chloroaniline.

A crystalline product was formed very easily and very quickly when diethyldithiophosphoric acid was reacted with p-chloroaniline. Crystalline products were similarly obtained by us with β-naphthylamine, with aniline and its derivatives (p-toluidine) and with 1,3,4-trimethylxylidine). According to their analyses they are all salts of diethyldithiophosphoric acid with aromatic amines (Table 3).

TABLE 3

Formula	Melting point	Phosphorus content (in %)		Yield (in %)
		Found	Calculated	
$p\text{-}ClC_6H_4NH_2 \cdot HSSP(OC_2H_5)_2$	120°	9.8, 9.9	9.8	71
$1,3,4\text{-}(CH_3)_3C_6H_3NH_2 \cdot HSSP(OC_2H_5)_2$	131.5-132	10.2, 10.2	10.0	95
$C_6H_5NH_2 \cdot HSSP(OC_2H_5)_2$	86	10.8, 11.1	11.1	83
$p\text{-}CH_3C_6H_4NH_2 \cdot HSSP(OC_2H_5)_2$	87-88	10.9, 10.5	10.6	85
$C_{10}H_7NH_2 \cdot HSSP(OC_2H_5)_2$	116-117	10.0, 9.6	9.7	87

The salts are white crystalline substances, soluble in alcohol, ether, benzene and toluene.

In respect of melting point and phosphorus content the salt of diethyldithiophosphoric acid with p-chloroaniline is identical with the product obtained by interaction of diethyldithiophosphoric acid with benzal-p-chloroaniline; a mixed sample did not give a melting point depression.

Benzal-p-chloroaniline gradually undergoes hydrolysis when kept and when reacted with diethyldithiophosphoric acid, due to the action of atmospheric moisture and the solvent, and p-chloroaniline and benzaldehyde are formed. Rapid formation of the salt of diethyldithiophosphoric acid with p-chloroaniline promotes displacement of the equilibrium to the right and acceleration of the process of hydrolysis during the reaction:

$$C_6H_5CH{=}NC_6H_4Cl + H_2O \rightleftharpoons C_6H_5CHOHNHC_6H_4Cl \rightleftharpoons C_6H_5CHO +$$

$$+ H_2NC_6H_4Cl \xrightarrow{+(C_2H_5O)_2PSSH} ClC_6H_4NH_2 \cdot HSSP(OC_2H_5)_2.$$

Subsequently, therefore, we carried out the synthesis of anils and the addition to them of diethyldithiophosphoric acid under conditions excluding the presence of moisture in the reaction mixtures. The full mixed esters of dithiophosphoric acid were prepared from benzal-p-chloroaniline, p-methyl-benzal-p-chloroaniline and diethyldithiophosphoric acid in good yields (80-90%).

EXPERIMENTAL

Procedure for addition of dialkylthiophosphorous acids to anils. To an equimolar mixture of the anil and the dialkylthiophosphorous acid, dissolved in a little ethyl alcohol and placed in a round-bottomed flask, was added a few drops of sodium alkoxide. In the case of diethylthiophosphorous acid the ethoxide was used, and in the case of dibutylthiophosphorous acid sodium butoxide was used. Scarcely any heat was developed by the reaction mixtures. After heating on a water bath for 20-30 minutes, the reaction mixtures were run into porcelain dishes and left to crystallize. In some cases crystallization set in very quickly, even during cooling of the reaction mixtures; in others it only set in after some days. The products were purified by two or three recrystallizations from ethyl alcohol. The characteristics of the synthesized esters of aminothiophosphinic acids are given in Table 1.

Procedure for addition of diethyldithiophosphoric acid to anils. The reactions were carried out with equimolar amounts of anils and diethyldithiophosphoric acid in solution in ethyl alcohol. The solution of anil in alcohol was put into a round-bottomed flask equipped with dropping funnel and reflux condenser, and diethylthiophosphoric acid was slowly introduced dropwise. Heat was developed. The reaction flask was cooled in an ice bath. After addition of the calculated amount of diethyldithiophosphoric acid, the reaction mixture was heated on a water bath for 10-15 minutes and poured into a porcelain dish. Crystallization started quickly in some experiments; in others it was completed in a few hours. The crystalline mass was filtered on a porous filter and recrystallized several times from ethyl alcohol. The full mixed esters of dithiophosphoric acid are yellow crystalline substances; most of them are soluble in alcohol, ether, dioxane, benzene and toluene. Some are soluble in hot water. The characteristics of the products are set forth in Table 2.

Addition of diethyldithiophosphoric acid to benzal-p-chloroaniline. 1. Benzal-p-chloroaniline was prepared by the usual procedure from benzaldehyde and p-chloroaniline in ethyl alcohol solution. To a solution of 1.45 g

benzal-p-chloroaniline in 4.5 ml ethyl alcohol was added dropwise 1.2 g diethyldithiophosphoric acid. The mixture was well stirred and run into a porcelain dish for crystallization. Crystallization commences after 10-15 minutes. After an hour the yellow crystalline mass was collected on a porous filter and recrystallized several times; first from alcohol and then from benzene. Yield 0.8 g with m. p. 119-120°.

Found %: P 9.60, 9.91. $C_{17}H_{21}O_2NS_2PCl$. Calculated %: P 7.72. $C_{10}H_{17}O_2NS_2PCl$. Calculated %: P 9.88.

2. In an Arbuzov flask, fitted with dropping funnel and sloping condenser, was placed 2.07 g p-chloroaniline and 7 ml anhydrous toluene. After the p-chloroaniline had dissolved, a solution of 1.75 g benzaldehyde in 3.5 ml toluene was slowly added with continuous stirring of the reaction mixture. After brief heating on a water bath, a part of the toluene together with the water of reaction was distilled off at a residual pressure of 100 mm. After the residue had been cooled, 3 g diethyldithiophosphoric acid was gradually added. The reaction mixture was stirred a few minutes and the viscous, dark-red oil was then run into a porcelain dish and left to crystallize in a vacuum desiccator. Yield 6.3 g crystals melting after recrystallization from toluene at 96-97°.

Found %: P 7.39, 7.69. $C_{17}H_{21}O_2NS_2PCl$. Calculated %: P 7.72.

Addition of diethyldithiophosphoric acid to p-methylbenzal-p-chloroaniline. To a solution of 2 g p-methylbenzal-p-chloroaniline in 4 ml ethyl alcohol was added 1.8 g diethyldithiophosphoric acid. The reaction mixture was heated 1 hour on a water bath and then left to crystallize in a porcelain dish in the open air. After 24 hours, nearly the whole of the contents of the dish had crystallized. The crystalline mass was heterogeneous — a mixture of fine yellow and white crystals. In the course of several recrystallizations the amount of yellow crystals became smaller and smaller. Finally, 1.5 g white crystals with m. p. 120° was obtained.

Found %: P 9.82, 9.89. $C_{18}H_{23}O_2NS_2PCl$. Calculated %: P 7.46. $C_{11}H_{19}O_2NS_2PCl$. Calculated %: P 9.46.

To a solution of 1.23 g p-chloroaniline in 4.06 g toluene was gradually added 1 g p-tolualdehyde in 4 ml toluene. The reaction mixture was heated 10 minutes on a water bath, after which a portion of the toluene and water was distilled off from the reaction mixture. To the dehydrated solution was added 1.65 g diethyldithiophosphoric acid, and the reaction mixture was then heated for a short period on a water bath before leaving to crystallize in a vacuum desiccator. Yield 3.2 g perfectly homogeneous yellow crystals with m. p. 96°.

Found %: P 8.01, 7.70. $C_{18}H_{23}O_2NS_2PCl$. Calculated %: P 7.46.

Procedure for preparation of salts of diethyldithiophosphoric acid with aromatic amines. Equimolar amounts of diethyldithiophosphoric acid and aromatic amine were reacted in toluene solution with stirring. Salts were formed very quickly and separated from solution in the form of white crystals. The salts were recrystallized from toluene. Most of them were soluble in alcohol, toluene and ether. Their characteristics are given in Table 3.

Reaction between diethyldithiophosphoric acid and benzaldehyde. To 2.29 g benzaldehyde was added 4 g diethyldithiophosphoric acid. The temperature of the reaction mixture rose from 13 to 21°. After addition of a few drops of sodium ethoxide the temperature rose to 35°. The reaction mixture was heated on a water bath 15 minutes and then left to crystallize in a porcelain dish. Crystallization took place very slowly. After 24 hours 1 g hydroxybenzyldiethyldithiophosphoric acid with m. p. 104° was obtained. The product dissolves readily in benzene, dioxane and alcohol.

Found %: P 11.06. $C_{11}H_{17}O_3PS_2$. Calculated %: P 10.62.

SUMMARY

1. Addition of dialkylthiophosphorous acids to anils containing various substituted groups in one and both benzene rings gave a whole series of derivatives of dialkyl esters of N,C-diphenylaminomethylthiophosphinic acid.

2. A procedure was developed for carrying out the addition of diethyldithiophosphoric acid to anils. A series of derivatives of N,C-diphenylaminomethyldiethyl esters of dithiophosphoric acid was synthesized.

3. It was shown that diethyldithiophosphoric acid readily forms salt-like compounds with aromatic amines.

4. It was shown that diethyldithiophosphoric acid adds on to aldehydes of the aromatic series with formation of hydroxybenzyldiethyl esters of dithiophosphoric acid.

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SYNTHESIS OF POLYNUCLEAR KETONES

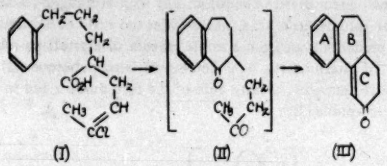
IX. 2-KETO-2,3,4,4a,6,7-HEXAHYDRO-5H-DIBENZ-(a,c)-CYCLOHEPTATRIENE

G. T. Tatevosyan, A. G. Terzyan, S. A. Vardanyan and A. G. Vardanyan

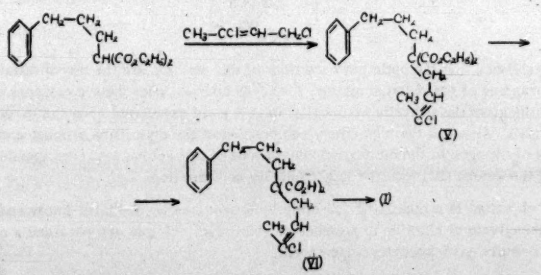
It has been shown [1] that γ-phenylbutyric acids containing a 3-chlorocrotyl radical in the α-position to the carboxyl group are subjected on reaction with sulfuric acid to successive hydrolysis, intramolecular acylation and intramolecular crotonic condensation with formation of tricyclic ketones of the phenanthrene series.

In the present paper is described the application of this scheme to the synthesis of a tricyclic ketone with a seven-membered B chain – 2-keto-2,3,4,4a,6,7-hexahydro-5H-dibenz-(a,c)-cycloheptatriene (III). It seems to us that this ketone may be of interest as starting point for synthesis of compounds similar in structure of ring skeleton to the alkaloid colchicine and its analogs.

It was proposed to prepare the tricyclic ketone (III) by hydrolysis and double cyclization of α-(3-chlorocrotyl)-phenylvaleric acid (I):



The starting acid (I) was obtained by the malonic synthesis from 1,3-dichloro-2-butene and γ-phenylpropyl bromide prepared by reduction of ethyl cinnamate followed by conversion of phenylpropyl alcohol to the bromide:



Intramolecular acylation of δ-phenylvaleric acids to benzosuberones proceeds, as we know, with very much greater difficulty, under more drastic conditions and usually in lower yields than the analogous reactions of formation of α-tetralones and hydrindones from the corresponding γ-phenylbutyric and β-phenylpropionic acids. Up to a few years ago the cyclization of δ-phenylvaleric acids was effected predominantly by dehydrochlorination of their acid chlorides in presence of aluminum chloride [2] or tin chloride [3]; more rarely the free acids were cyclized with the help of phosphorus pentoxide [3, 4].

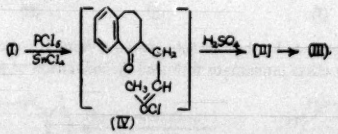
The fact that sulfuric acid had not been used for these purposes was probably due to the above-noted difficulty of cyclization of δ-phenylvaleric acids and the predominance of the process of their sulfonation; it was therefore to be expected that in this case a single-step transformation of the original acid (I) into the tricyclic ketone (III) would

be impossible or, at the best, would lead to very low yields. Indeed, repreated attempts to realize this transformation showed that reaction of acid (I) with sulfuric acid leads exclusively to sulfonation, the tricyclic ketone not being formed. It was therefore necessary to effect the intramolecular acylation with the help of another cyclization agent, and consequently to effect the synthesis of ketone (III) by separate closures of rings B and C.

The most convenient agent for intramolecular acylation of δ-phenylvaleric acids, is,as we know, polyphosphoric acid, which has found wide application in recent years. However, contrary to expectations, the application of this agent in the present case did not give positive results. Interaction of polyphosphoric acid with acid (I) is accompanied by evolution of hydrogen chloride, pointing to occurrence of a side reaction at the expense of the 3--chlorocrotyl radical. A neutral product was obtained in minute yield (up to 5.5%), while the main bulk of product isolated from the reaction was an acidic substance which could not be the original acid in the pure state since, as noted above, hydrogen chloride was given off during the reaction. This product was not examined since experiments on cyclization with polyphosphoric acid, which failed to give the desired results, were abandoned.

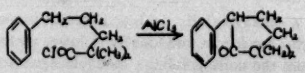
More positive results were got by cyclization of the chloride of acid (I) with the help of tin chloride in benzene solution. By changing the reaction conditions it was found that in presence of a large excess of tin chloride and with boiling of the reaction mixture, a neutral product of reaction, a crude and evidently very impure benzosuberone (IV), is formed in yields reaching 40.5% of the theoretical. The unreacted portion of the original acid, constituting about half of that taken into the reaction, was recovered in the fairly pure state and could be used in a fresh experiment.

The substituted benzosuberone (IV), however, could not be obtained in the pure state since it could not be crystallized out from the neutral product, while serious decomposition occurred on distillation in vacuum; sulfuric acid treatment was therefore applied to the unpurified, oily substance remaining after removal of the ether from the solution of the neutral product of cyclization of acid (I) chloride. The results of these experiments were greatly affected by the reaction conditions: under drastic conditions and with prolonged (3 days) interaction the compound formed almost completely a water-soluble sulfo acid, while under too mild conditions and with shorter period of action of sulfuric acid, the main product (apart from a small amount of crystalline substance) was an oil evidently containing a considerable amount of intermediate 2-(γ-ketobutyl)-benzosuberone (II) which had not undergone the crotonic condensation. Further treatment with sulfuric acid of the oily product led to part formation of a crystalline substance identified as the tricyclic ketone (III):



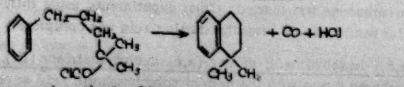
It was established that the optimum conditions of this reaction are the use of sulfuric acid of specific gravity 1.76-1.78 and standing of the reaction mixture for 24-48 hours. Under these conditions the neutral product of the preceding reaction gives the tricyclic ketone (III) in 25% yield calculated upon the crude, unpurified substituted benzosuberone (IV). Although the elementary composition of the crystalline product corresponded to formula (III) and the content of nitrogen in the dinitrophenylhydrazone of this ketone also corresponded to the calculated amount, the structure of the ketone (III) required supplementary confirmation.

With the objective of synthesizing 2,2-dimethylbenzosuberone, Ramarth-Lucas and Hoch [5] cyclized α,α--dimethyl-δ-phenylvaleryl chloride in presence of aluminium chloride and obtained a compound which they assumed to be 2,2-dimethyl-5-phenylcyclopentanone:

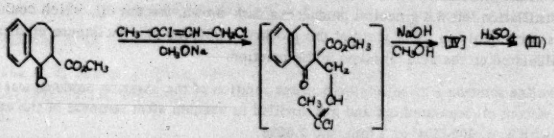


The authors not only failed to submit any proof of this structure but omitted to describe the properties and preparation of the compound, so that justifiable doubts about the correctness of their conclusion must be aroused. Since, however, we did not find in the literature any other examples of cyclization of α-substituted δ-phenylvaleric acids, it was impossible to rule out the possibility of an analogous transformation of acid (I) with formation of phenyltetrahydrohydrindone. When our investigation was completed a paper [6] was published which also dealt with

the cyclization of α-α-dimethyl-δ-phenylvaleryl chloride with aluminium chloride; this work indicated partial destruction with evolution of carbon monoxide and formation of 1,1-dimethyl-1,2,3,4-tetrahydronaphthalene:



The starting substance in the second synthesis of ketone (III) was 2-carbomethoxybenzosuberone [7]. Condensation of this β-ketoester with dichlorobutene followed by saponification and decarboxylation gave the substituted benzosuberone (IV). In this case, again, the substance was subjected to the action of sulfuric acid without previous purification. A 56% yield was obtained of the tricyclic ketone (III), which proved to be identical with the preparation obtained by the route described above; both specimens had m. p. 100-101°, and their mixture melted without depression.



The second synthesis of ketone (III), carried out with the objective of confirming the structure of this compound, proved to be more convenient than the first method of preparation; the second method gives the intermediate substituted benzosuberone (IV) in higher yield and in a purer form, as evidenced by the doubled yield of the product of sulfuric acid hydrolysis and cyclization.

The synthesis of ketones of this series and some of their transformations will be the subject of a further investigation.

EXPERIMENTAL

The starting γ-phenylpropylmalonic ester, obtained in 72.8% yield by condensation of γ-phenylpropyl bromide with malonic ester [8], had the following properties: b. p. 170-173° at 8 mm, d_4^{18} 1.0546, n_D^{18} 1.4901.

[(γ-Chloro)-crotyl-(γ-phenyl)-propyl]-malonic ester (V). To a solution of the sodium derivative of γ-phenylpropylmalonic ester, prepared from 120 g of this ester and 10 g sodium in 160 ml anhydrous alcohol, was added 65 g dichlorobutene, and the mixture was boiled on a water bath for 6 hours. After the alcohol had been driven off, acidified water was added; the substance was dissolved in ether, the solution was washed with water and dried with sodium sulfate. Vacuum distillation gave 132 g (83.56%) light-yellow oil with b. p. 194-200° at 5 mm.

d_4^{19} 1.0970, n_D^{19} 1.5038, MR_D 98.89. Calc. 98.66.

Found %: Cl 9.39. $C_{20}H_{27}O_4Cl$. Calculated %: Cl 9.68.

[(γ-Chloro)-crotyl-(γ-phenyl)-propyl]-malonic acid (VI). A mixture of 131 g of the disubstituted malonic ester (V), 650 ml 90% alcohol and 43 g sodium hydroxide was boiled 4 hours, after which 400 ml water was added and the alcohol completely distilled off. Acidification of the cooled residue led to separation of a heavy oil which crystallized on standing. The compound was filtered, washed with water and dried. After thorough washing with a mixture of benzene and ligroine, 80 g (72%) of a white crystalline powder with m. p. 124-125° was obtained.

Found %: Cl 11.40, 11.13. $C_{16}H_{19}O_4Cl$. Calculated %: Cl 11.43.

α-(3-Chlorocrotyl)-δ-phenylvaleric acid (I). 57 g pure disubstituted malonic acid (VI) was subjected to decarboxylation by heating. The oil obtained was distilled in vacuum to give 45 g (91.98%) nearly colorless, viscous oil with b. p. 190-195° at 4 mm; n_D^{20} 1.5298. On standing it crystallized completely; m. p. 39-40°.

Found %: Cl 13.43, 12.93. $C_{15}H_{19}O_2Cl$. Calculated %: Cl 13.30.

Reaction of acid (I) with sulfuric acid. 1.33 g of the substituted valeric acid was treated with 7.5 ml sulfuric acid (s. g. 1.78). The reaction mixture, which gave off hydrogen chloride and was stirred from time to time, was stood at room temperature until the crystalline substance dissolved completely; it was then heated on a water bath in a stream of carbon dioxide at 60° for 2 1/2 hours. The next day the mixture was poured onto iced water but no insoluble substance separated out. The acid solution was treated with ether, the ether was washed with caustic alkali to remove acid products, then washed with water and dried. No residue remained after removal of the ether.

The alkaline washed solution was acidified and treated with ether. Removal of the ether from the dried solution left a few drops of oil. Since the substance might have been a keto acid, an attempt was made to prepare the semicarbazone, but no semicarbazone was formed. Other experiments, using sulfuric acid of s. g. 1.78 and 1.74 at room temperature, had similar results; in all cases the starting acid was completely sulfonated.

2-Keto-2,3,4,4a,6,7-hexahydro-5H-dibenz-(a,c)-cycloheptatriene (III). a) As indicated above, an attempt to close the seven-membered B ring with the help of polyphosphoric acid as reported in the literature [9] ended in failure. After a number of experiments the following conditions of cyclization of acid (I) chloride were adopted: to a solution of acid (I) chloride, prepared by reaction of 9 g acid with 7.1 g phosphorus pentachloride in 45 ml dry benzene was added a solution of 40 g tin chloride in 150 ml benzene with cooling and stirring. After brief standing at room temperature, the mixture was gently boiled for 6 hours. The darkened solution was decomposed and washed several times with hydrochloric acid, then with alkali and water and dried with sodium sulfate. Removal of the benzene by distillation left 3.4 g neutral product – a dark-brown, viscous oil, which could not be distilled in vacuum due to serious decomposition. The yield of this product, consisting of very impure substituted benzosuberone (IV), was 40.5% calculated on the acid (I) taken in the reaction.

The alkaline solution with which the benzene solution of the reaction products was washed, was acidified; a light-brown, viscous oil separated out and was distilled in vacuum after removal of the ether. Yield 5 g unreacted starting acid with b. p. 202-204° at 7 mm, n_D^{18} 1.5298.

To the neutral product of the preceding reaction (3.4 g) was gradually added 11 ml sulfuric acid (s. g. 1.78). The reaction mixture, which gave off hydrochloric acid, was left at room temperature for 48 hours, and then poured on to iced water; the resultant semi-crystalline mass was dissolved in ether, the solution was washed with alkali for removal of acid products, then washed with water and dried. The ether was removed to leave a yellow crystalline substance. It was recrystallized from ether (boiling with charcoal) to form colorless needles melting at 100-101°. Yield 0.83 g [25.15% reckoned on the 3.4 g of substituted benzosuberone (IV)].

Found %: C 84.56, 85.03; H 7.77, 7.93. $C_{15}H_{16}O$. Calculated %: C 84.85; H 7.60.

The orange-red 2,4-dinitrophenylhydrazone had m. p. 183-185° after several recrystallizations from alcohol.

Found %: N 14.63, 14.63. $C_{21}H_{20}O_2N_4$. Calculated %: N 14.29.

b) The starting 2-carbomethoxy-5,6-benzosuberone was prepared, in accordance with the literature procedure [7], by condensation of benzosuberone with methyl oxalate in presence of sodium methoxide followed by closure of the enol-lactone ring and decarboxylation of the substituted methyl glyoxylate.

To sodium methoxide, prepared by dissolving 5.7 g sodium in 110 ml anhydrous methanol, was added 60 ml dry benzene and 10.8 g 2-carbomethoxybenzosuberone. The mixture was boiled 30 minutes, then cooled; dropwise addition was then made in the course of 25 minutes of 33.5 ml dichlorobutene. After 30 minutes' boiling, the mixture was cooled and acidified with acetic acid; the greater part of the solvent was removed by heating in vacuum. To the residue was added 50 ml benzene and water until the salt precipitate had dissolved completely. The benzene solution was washed with alkali, then with water and dried. The benzene was taken off by gentle heating in vacuum; addition was made to the residue of 40 ml dry toluene for removal of excess dichlorobutene as well as of a possible side product (methylchlorocrotyl ester), and this toluene was also completely removed by heating in vacuum.

The residue (15 g), consisting of 2-(γ-chlorocrotyl)-2-carbomethoxybenzosuberone, was hydrolyzed by boiling for 2 hours with a solution of 26.5 g sodium hydroxide in 45 ml water and 185 ml methyl alcohol. After removal of the greater part of the methyl alcohol in vacuum, the residue was acidified with dilute sulfuric acid; the product was dissolved in ether and the solution washed with water and dried. After removal of the ether, the substituted benzosuberone (IV) was obtained in the form of a light-brown, viscous oil in the amount of 12.17 g (98.8% reckoned on the original carbomethoxybenzosuberone).

4 g crude substituted benzosuberone (IV) was hydrolyzed and cyclized by the action of 10 ml sulfuric acid (s. g. 1.78) under the above-described conditions. Yield 1.92 g (56.3%) of needles which, after recrystallization from ether (boiling with charcoal), had m. p. 100-101°. A mixed sample with the above-described preparation of tricyclic ketone melted without depression.

Found %: C 85.05, 85.00; H 7.96, 7.81. $C_{15}H_{16}O$. Calculated %: C 84.85; H 7.60.

SUMMARY

1. α-(3-Chlorocrotyl)-δ-phenylvaleric acid (I) was synthesized and a study was made of the conditions of its hydrolysis and double cyclization to the 2-keto-hexahydrodibenzocycloheptatriene (III).

2. It was found that preparation of ketone (II) in a single step with the help of concentrated sulfuric acid cannot be realized due to complete sulfonation of the original acid. The tricyclic ketone was obtained by cyclization of acid (I) chloride with the help of tin chloride followed by reaction of the substituted benzosuberone (IV) with sulfuric acid.

3. The same ketone was prepared in higher yield from benzosuberone; this synthesis also confirmed its structure.

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IV. CYANINE DYES FROM DERIVATIVES OF 5- AND 6-TRIFLUOROMETHYLMERCAPTO-BENZOTHIAZOLES

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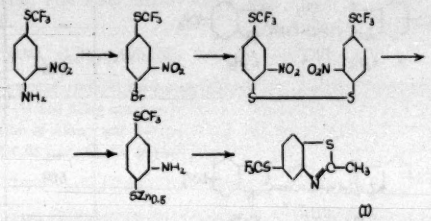
One of us [1] has described the synthesis of 2-methyl-6-trifluoromethylmercapto-benzothiazole and of some cyanine dyes from this base. In the present paper we describe a number of new cyanines from 2-methyl-6-trifluoromethylmercapto-benzothiazole, as well as the synthesis of its isomer which contains the trifluoromethylmercapto group in the 5-position, and of the corresponding dyes.

We synthesized 2-methyl-5-trifluoromethylmercapto-benzothiazole (I) from 3-nitro-4-aminophenyltrifluoromethyl sulfide [2] according to the scheme:



The prepared product melted at 93-94° or 20° higher than its isomer 2-methyl-6-trifluoromethylmercapto-benzothiazole. Both bases are converted into quaternary salts (ethyl tosylates). From the latter was synthesized a series of cyanine dyes. The structural formulas and absorption maxima of the new cyanine dyes are detailed in the table which also gives, for comparison, the absorption maxima of the corresponding dyes not containing SCF_3 groups. It is seen from the table that in thiacarbocyanines containing SCF_3 the absorption maxima are slightly displaced toward the red region of the spectrum in comparison with unsubstituted dyes; the displacement is 7 mμ on the average in the case of 5-trifluoromethylmercapto- and 10 mμ in that of 6-trifluoromethylmercapto- derivatives.

EXPERIMENT

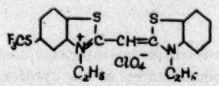
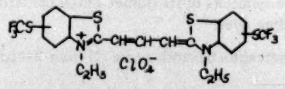
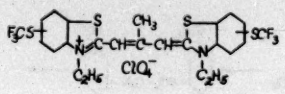
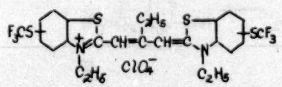
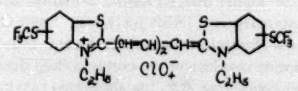
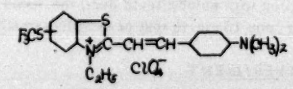
3-Nitro-4-aminophenyltrifluoromethyl sulfide was used with m. p. 85-86° [2].

3-Nitro-4-bromophenyltrifluoromethyl sulfide. 15 g 3-nitro-4-aminophenyltrifluoromethyl sulfide was dissolved in 40 ml sulfuric acid (d 1.84) by heating on a water bath. The solution was cooled, 60 ml water was added, and a solution of 5.6 g $NaNO_2$ in 10 ml water was slowly run in with stirring. The temperature during diazotization was held at 3-5°. The diazo solution was stirred 30 minutes at room temperature, filtered, and run dropwise into a boiling aqueous solution containing Cu_2Br_2 prepared in the usual way. The resultant bromo derivative was immediately distilled off in steam. The product was extracted from the distillate with benzene and the benzene solution was washed with sodium hydroxide (2 N), then with water, with concentrated sulfuric acid, and finally again with water until neutral to congo. The benzene was distilled off and the product vacuum-distilled. The distillate was a yellow oil with b. p. 121-123° at 5 mm.

4,4'-Bis-(trifluoromethylmercapto)-2,2'-dinitrodiphenyl disulfide. 4.8 g crystalline sodium sulfide was dissolved by heating on a water bath in 15 ml alcohol; 0.64 g sulfur was then added and the mixture heated another 30 minutes. The warm mixture was run into a solution of 12 g 3-nitro-4-bromophenyltrifluoromethyl sulfide in

30 ml alcohol, after which the solution was boiled on a water bath for 2 hours. The disulfide which came down on cooling was filtered and crystallized from glacial acetic acid. M. p. 133-134°. Yield 7 g (70%).

Found %: N 5.39, 5.60; S 25.19, 25.40. $C_{14}H_8O_4N_2F_6S_4$. Calculated %: N 5.51; S 25.2.

Preparation number	Formula of dye	γ max (in mμ)		
		6-substituted	5-substituted	dyes without SCF_3
(II)		–	430	422
(III)		–	560	558
(VIII)		568	–	
(IV)		–	550	544
(IX)		555	–	
(V)		–	555	550
(X)		558	–	
(VI)		–	658	651
(XI)		665	–	
(VII)		–	543	530

2-Methyl-5-trifluoromethylmercapto-benzothiazole (I). 6 g disulfide was dissolved in 50 ml glacial acetic acid with heating. To the solution was added, in small portions, 15.5 g zinc dust and 12 ml hydrochloric acid (d 1.19). The solution was filtered and diluted with water; then sodium acetate was added until the acid reaction to congo had disappeared, and the mixture was left to stand 2 hours. The precipitated zinc mercaptide was filtered and dried at 40°. Yield of dry product 6 g. It was heated to the boil with 18 ml acetic anhydride for 3 hours. The solution was then made alkaline and the product distilled with steam. The product crystallized in the receiver and was filtered and dried. Yield 3.5 g (60%). Recrystallization from ligroine gave colorless prisms with m. p. 93-94°.

Found %: N 5.57, 5.90; S 25.49, 25.62. $C_9H_6NS_2F_3$. Calculated %: N 5.62; S 25.70.

Ethoperchlorate of 2-methyl-5-trifluoromethylmercapto-benzothiazole was prepared from 0.32 g base and 0.32 g ethyl p-toluenesulfonate by heating 4 hours at 150°. After cooling, the product was washed with ether and dried. Quantitative yield. The ethoperchlorate was precipitated from aqueous solution by the action of $NaClO_4$. M. p. 138-139°.

The ethoperchlorate of 2-methyl-6-trifluoromethylmercapto-benzothiazole was similarly prepared from 0.5 g base and 0.5 g ethyl p-toluenesulfonate. Yield of product (after washing with ether and acetone) 0.8 g (90%), m. p. 153°.

[3-Ethyl-5-trifluoromethylmercapto-benzothiazole-(2)]-[3-ethylbenzothiazole-(2)]-methinecyanine perchlorate (II). 0.2 g ethyl p-toluenesulfonate of (I), 0.15 g ethyl ethosulfate of 2-methylmercapto-benzothiazole and 0.15 g anhydrous sodium acetate were boiled with 3 ml absolute alcohol for 45 minutes. After cooling, the solution was diluted with water. The dye was filtered and was precipitated from alcoholic solution with an aqueous solution of sodium perchlorate. Yellow needles from alcohol. Yield 0.06 g (50%), m. p. 266-267°. Absorption maximum 430 mμ.

Found %: S 17.71, 17.77. $C_{20}H_{18}N_2S_3F_3ClO_4$. Calculated %: S 17.84.

Bis-[3-ethyl-5-trifluoromethylmercapto-benzothiazole-(2)]-trimethinecyanine perchlorate (III). 0.18 g ethoperchlorate of (I) and 0.2 g ethyl orthoformate were boiled with 4 ml pyridine 25 minutes. After cooling, the dye came down. Bronze needles from alcohol. Decomp. p. 279-280°. Yield 0.08 g (51%). Absorption maximum 560 mμ.

Found %: S 19.38, 19.45. $C_{23}H_{19}N_2S_4O_4ClF_6$. Calculated %: S 19.26.

Bis-[3-ethyl-5-trifluoromethylmercapto-benzothiazole-(2)]-9-methyltrimethinecyanine perchlorate (IV). 0.25 g ethyl p-toluenesulfonate of (I) and 0.25 g ethyl orthoformate were boiled with 4 ml pyridine and 2 drops acetic anhydride for 45 minutes. The dye was precipitated with ether and was isolated from the alcoholic solution in the form of the perchlorate. Blue-black needles from alcohol. Yield 0.1 g (52%), decomp. p. 255-256°. Absorption maximum 550 mμ.

Found %: S 18.74, 18.93. $C_{24}H_{21}N_2S_4O_4ClF_6$. Calculated %: S 18.86.

Bis-[3-ethyl-5-trifluoromethylmercapto-benzothiazole-(2)]-9-ethyltrimethinecyanine perchlorate (V). 0.2 g ethyl p-toluenesulfonate of (I) and 0.2 g ethyl orthoformate were boiled 10 minutes with 2 ml pyridine. The dye was brought down by addition of water, and was isolated as the perchlorate from alcoholic solution. It was crystallized from alcohol. Yield 0.05 g (33%), m. p. (decomp.) 235-236°. Absorption maximum 555 mμ.

Found %: S 18.57, 18.70. $C_{25}H_{23}N_2S_4O_4ClF_6$. Calculated %: S 18.48.

Bis-[3-ethyl-5-trifluoromethylmercapto-benzothiazole-(2)]-pentamethine-cyanine perchlorate (VI). 0.2 g ethyl p-toluenesulfonate of (I) and 0.06 g β-anilinoacrolein anil hydrochloride were boiled 30 minutes with 2 ml acetic anhydride and 3 drops pyridine. The dye was brought down with ether and separated from the alcoholic solution as the perchlorate. It was crystallized from alcohol. Yield 0.07 g (45%), decomp. p. 250-251°. Absorption maximum 658 mμ.

Found %: S 18.35, 18.38. $C_{25}H_{21}N_2O_4S_4ClF_6$. Calculated %: S 18.55.

Ethoperchlorate of 2-p-dimethylaminostyryl-5-trifluoromethylmercapto-benzothiazole (VII). 0.08 g ethoperchlorate and 0.06 g p-dimethylaminobenzaldehyde were boiled with 2 ml acetic anhydride for 30 minutes. After cooling, the precipitate of dye was filtered, washed with ether, and crystallized from alcohol. Yield 0.09 g (81%), m. p. 232-233°. Absorption maximum 545 mμ.

Found %: S 12.42, 12.50. $C_{20}H_{20}O_4N_2S_2ClF_3$. Calculated %: S 12.58.

Bis-[3-ethyl-6-trifluoromethylmercapto-benzothiazole-(2)]-trimethinecyanine perchlorate (VIII). 0.25 g ethyl p-toluenesulfonate of 2-methyl-6-trifluoromethylmercapto-benzothiazole and 0.25 g ethyl orthoformate were boiled with 3 ml acetic anhydride for 30 minutes. The dye was precipitated with ether and isolated from alcoholic solution as the perchlorate. It was crystallized from alcohol. Yield 0.09 g (50%), decomp. p. 287-288°. Absorption maximum 568 mμ.

Found %: S 19.10, 19.30. $C_{23}H_{19}N_2S_4O_4ClF_6$. Calculated %: S 19.26.

Bis-[3-ethyl-6-trifluoromethylmercapto-benzothiazole-(2)]-9-methyltrimethinecyanine perchlorate (IX). 0.2 g ethyl p-toluenesulfonate of 2-methyl-6-trifluoromethylmercapto-benzothiazole and 0.2 g ethyl orthoformate were boiled with 2 ml pyridine and 2 drops acetic anhydride 40 minutes. The product was worked up and purified as in the preceding preparation. Yield 0.06 g (40%), decomp. p. 250-251°. Absorption maximum 555 mμ.

Found %: S 18.65, 18.99. $C_{24}H_{21}N_2O_4S_4ClF_6$. Calculated %: S 18.86.

Bis-[3-ethyl-6-trifluoromethylmercapto-benzothiazole-(2)]-9-ethyltrimethinecyanine perchlorate (X). 0.2 g ethyl p-toluenesulfonate of 2-methyl-6-trifluoromethylmercapto-benzothiazole and 0.2 g ethyl orthoformate were boiled with 1 ml pyridine for 1 minute. If the solution was boiled for 3-5 minutes the dye was decolorized. Further treatment as before. Yield 0.05 g (35%), decomp. p. 220-221°. Absorption maximum 558 mμ.

Found %: S 18.28, 18.30. $C_{25}H_{23}O_4N_2S_4ClF_6$. Calculated %: S 18.48.

Bis-[3-ethyl-6-trifluoromethylmercapto-benzothiazole-(2)]-pentamethinecyanine perchlorate (XI). 0.2 g ethyl p-toluenesulfonate of 2-methyl-6-trifluoromethylmercapto-benzothiazole and 0.06 g β-anilinoacrolein anil hydrochloride were boiled 30 minutes with 2 ml acetic anhydride and 3 drops pyridine. Further treatment as above. Yield 0.06 g (40%), decomp. p. 260-261°. Absorption maximum 665 mμ.

Found %: S 18.38. $C_{25}H_{21}N_2S_4O_4ClF_6$. Calculated %: S 18.55, 18.46.

SUMMARY

1. Syntheses were effected of 2-methyl-5-trifluoromethylmercapto-benzothiazole and of a series of intermediate compounds needed for its preparation.

2. Syntheses were effected of 6 thiacyanine dyes containing SCF_3 groups in the 5-position of the benzothiazole rings and 4 thiacyanine dyes containing SCF_3 groups in the 6-position.

3. The absorption maxima of thiacarbocyanines with the SCF_3 group as substituent in the 5,5'- or 6,6'-positions are displaced by an average of 7-10 mμ to the infrared portion of the spectrum by comparison with unsubstituted dyes.

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* T. p. = C. B. Translation pagination.

A NEW SYNTHESIS OF IRONES

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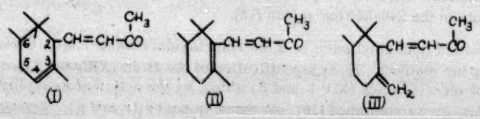
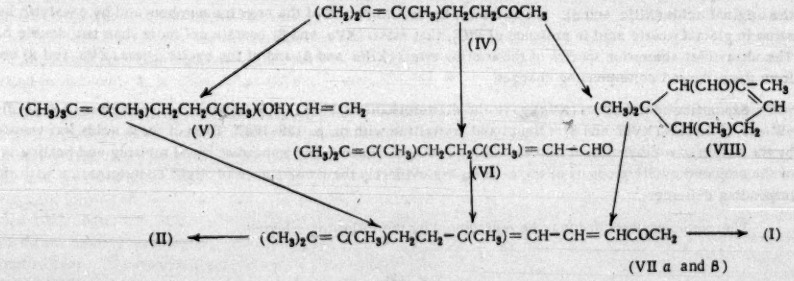
S. A. Elkina and N. A. Preobrazhensky

The sole source of irone at the present time is orris oil, which is isolated from the roots of various varieties of iris in a yield not exceeding 0.3%. The irone content of this oil is not more than 5% [1]. Natural irone is a mixture of isomers differing in the relative position of the double bonds and in steric structure: α-irones (I), β-irones (II) and γ-irones (III) [2, 3].



Four racemic isomers of α-irone are possible. Three optically active isomers have been isolated from natural α-irone. Three racemates have been prepared synthetically [4]. Synthesis of the optically active isomers has not yet been realized.

All the routes to synthesis of racemic irones known at the present time [5-13] may be generalized in the following scheme:

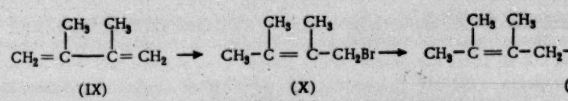


2,3-Dimethylhept-2-en-6-one (IV) is converted via a series of intermediate compounds into 3-methyllinalool (V) or 3-methylcitral (VI), and then into pseudoirone (VII). Cyclization of the latter with acidic agents [8-11] gives a mixture of isomeric α- and β-irones. Details have also been publsihed of the synthesis of irone from 2,3-dimethylhept-2-en-6-one (IV) via the step of methylcyclocitral (VIII) [7].

The disadvantage of all the known routes to irone, apart from the many steps, is the variability of the results obtained in the step of selective hydrogenation.

In this paper we describe a new synthesis of irones which does not involve a selective hydrogenation step.

The starting substance for the synthesis is 2,3-dimethylhept-2-en-6-one (IV), which was obtained in 63.5% yield (calculated on the 2,3-dimethyl-1,3-butadiene) by the literature method starting from pinacone hydrate and through the intermediates pinacone, 2,3-dimethyl-1, 3-butadiene (IX), 1-bromo-2,3-dimethyl-but-2-ene (X) and 2,3-dimethylbutenyl-2-acetoacetic ester (XI) [8], according to the scheme:



We employed the S. N. Reformatsky reaction with γ-bromocrotonic ester [14] for passage from 2,3-dimethylhept-2-en-6-one (IV) to the ester of 6-hydroxy-2,3,6-trimethyldecatrien-2,8-oic-(10) acid (XII). This condensation, unlike previously described syntheses of irone, also simultaneously ensures the necessary length of the hydrocarbon chain of 2,3-dimethylhept-2-en-6-one (IV) and the creation of double bonds in the positions required for the molecule of the pseudoirones (VII α and β) being synthesized.

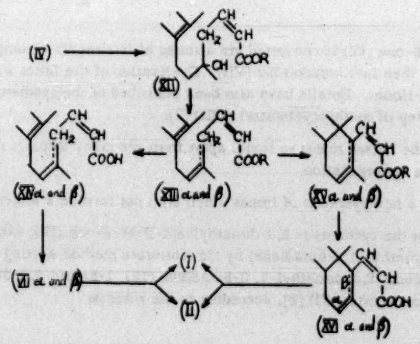
On dehydration of the hydroxy ester (XII) with phosphorus oxychloride in presence of pyridine, the ethyl ester of 2,3,6-trimethyldecatrien-2,5,8-oic-(10) acid was obtained (XIIIα), while dehydration with acetic anhydride or p-toluenesulfonic acid gave predominantly the compound with the other disposition of the double bonds – the ethyl ester of 2,3,6-trimethyldecatriene-2,6,8-oic-(10) acid (XIII β). The ultraviolet absorption spectrum of ester (XIIIα) does not contain a maximum in the 240-300 mμ region [15].

We realized the transition from ethyl esters of 2,3,6-trimethyldecatriene-2,5(6), 8-oic-(10) acids (XIIIα and β) to α-irones and β-irones by two methods. 1) By saponification of the esters (XIIIα and β) we obtained 2,3,6-trimethyldecatriene-2,5(6), 8-oic-(10) acids (XIV α and β) which, by the action of methyllithium (or dimethylcadmium) on the acid chlorides, were transformed [16] into pseudoirones (VIIα and β). Treatment of the latter with phosphoric acid gave a mixture of isomeric racemic α-irones (I), while treatment with sulfuric acid gave a mixture of β-irones (II). 2) The ethyl ester of 2,3,6-trimethyldecatriene-2,5,8-oic-(10) acid (XIII), by the action of phosphoric acid under the conditions of isomerization of pseudoirone (VIIα) into α-irones (I), was transformed into a mixture of the ethyl esters of diastereoisomeric 3'-(1,1,3,6-tetramethylcyclohexen-3,4-yl-2)-propen-2'-oic-(1') acids (XVα), while treatment with sulfuric acid, by the procedure for preparation of β-irones, gave a mixture of esters of the corresponding 3'-(1,1,3,6-tetramethylcyclohexen-2,3-yl-2)-propen-2'-oic-(1') acids (XV β).

The prepared compounds (XVα and β) differed in physico-chemical constants both from one another and from the original acids (XIIIα and β). It was shown, by determination of the bromine numbers and by catalytic hydrogenation in glacial acetic acid in presence of PtO_2, that esters (XVα and β) contain not more than two double bonds. The ultraviolet absorption spectra of the starting esters (XIIIα and β) and of the cyclic esters (XVα and β) obtained from them showed corresponding changes.

Saponification of esters (XVα) gave the diasteroisomeric 3'-(1,1,3,6-tetramethylcyclohexen-3,4-yl-2)-propen-2'-oic-(1') acids (XVIα and β) – liquid and crystalline with m. p. 159-164°. Each of these acids was transformed by the action of methyllithium into the corresponding α-irones. The somewhat broad melting and boiling ranges of the prepared cyclic products of the α-series are evidently the consequence of slight contamination with the corresponding β-isomers.

The syntheses described may be represented by the following scheme:



The presence in this scheme of the cyclic diastereoisomeric acids (XVI*a* and β) opens up the possibility of their resolution into the antipodes and consequently makes possible the synthesis of optically active irones.

EXPERIMENTAL

1. Ethyl ester of 6-hydroxy-2,3,6-trimethyldecadien-2,8-oic-(10) acids (XII). A mixture of 8.0 g (0.057 mole) 2,3-dimethylhept-2-en-6-one and 11 g (0.057 mole) ethyl γ-bromocrotonate, dissolved in 10 ml dry benzene, was run with stirring into 1.4 g (0.057 g-atom) fine magnesium shavings under a layer of 15 ml dry boiling benzene. After addition of 1/3 of the solution the start of the reaction was awaited; the remainder of the mixture was added dropwise in the course of 30 minutes. Boiling of the mixture was maintained through the heat of the reaction. For completion of the condensation the reaction mass was heated by gentle boiling of the solvent for 45 minutes. The reaction product was acidified with 10% glacial acetic acid; two layers then formed. The upper layer was collected and the lower one was extracted with benzene. The residue, after distillation of the solvent, was distilled in vacuum; b. p. 122-126° at 0.4 mm; 132-137° at 2mm. Yield 8.4 g (57.9%).

d_4^{20} 0.9905, n_D^{20} 1.4841; MR_D 73.38, $C_{15}H_{26}O_3$ F 2. Calc. 73.72.

Found %: C 70.89, 70.31; H 10.31, 10.31. $C_{15}H_{26}O_3$. Calculated %: C 70.84; H 10.30.

2. Ethyl esters of 2,3,6-trimethyldecatriene-2,5(6),8-oic-(10) acids (XIII*a* and β). 1) To a solution of the ethyl ester of 6-hydroxy-2,3,6-trimethyldecadiene-2,8-oic-(10) acid in 50 ml benzene was added 4 ml phosphorus oxychloride and 20 ml pyridine. The reaction mass was heated 45 minutes with gentle heating of the benzene, and the cooled solution was then run into water. The reaction product was extracted with benzene, and the residue after removal of the solvent was distilled in vacuum.

1st fraction b. p. 98-102° at 0.2 mm. Yield 75.2%; d_4^{20} 0.9457, n_D^{20} 1.4938, MR_D 72.63. $C_{15}H_{24}O_2$ F 3. Calc. 71.72.

Found %: C 76.07. $C_{15}H_{24}O_2$ 3. Calc. 71.72.

2nd fraction b. p. 105-107° at 0.2 mm; d_4^{20} 0.9483, n_D^{20} 1.5003, MR_D 73.23.

2) Into a flask with a reflux condenser, attached via a water separator, were charged 3 g ethyl ester of 6--hydroxy-2,3,6-trimethyldecadiene-2,8-oic-(10) acid, 50 ml dry benzene and 0.1 g p-toluenesulfonic acid (dried in a vacuum desiccator), and the mixture heated until cleavage of water was complete. The cooled reaction mass was washed with saturated aqueous sodium bicarbonate solution. The benzene was distilled off and the residue distilled in vacuum. B. p. 110-112° at 0.3 mm. Yield 2 g (71.7%).

3) A mixture of 3 g (0.012 mole) ethyl ester of 6-hydroxy-2,3,6-trimethyldecadiene-2,8-oic-(10) acid and 10.2 g (0.1 mole) freshly distilled acetic anhydride was kept at a gentle boil for 1 hour, after which the excess of acetic anhydride and the acetic acid formed were distilled off under reduced pressure. To the residue was then added 0.25 g (0.003 mole) freshly fused potassium acetate. The reaction mass was heated and at the same time the acetic acid formed during the reaction was distilled off. The vapor temperature during the distillation should not exceed 140°. After the acetic acid distillation was completed, a white flocculent precipitate of potassium acetate came down; heating was then stopped. After cooling, the reaction product was extracted with ether and dried with sodium sulfate. The ether was driven off and the residue distilled in vacuum. B. p. 126-130° at 2 mm. Yield 1.96 g (70.3%).

d_4^{20} 0.9749, n_D^{20} 1.4925, MR_D 70.40. $C_{15}H_{24}O_2$ F 3. Calc. 71.72.

3. 2,3,6-Trimethyldecatriene-2,5(6), 8-oic-(10) acids (XIV*a* and β). Into sodium ethoxide, prepared from 6 ml anhydrous ethanol and 0.27 g (0.012 g-atom) sodium, was run 0.21 ml (0.012 mole) water followed by 3 g (0.012 mole) ethyl ester of 2,3,6-trimethyldecatriene-2,5,8-oic(10) acid [or the ethyl ester of 2,3,6-trimethyl-decatriene-2,6,8-oic-(10) acid]. The mixture was heated 12 hours on a water bath, The resultant viscous oil was dissolved in water and extracted with ether to remove the unsaponified portion. After acidification of the aqueous layer with 10% sulfuric acid, the substance was extracted with ether and dried with sodium sulfate. The percentage of active hydrogen was determined in the substance remaining after distillation of the solvent. Yield 2.27 g (86.9%).

Found %: H 0.44. $C_{13}H_{20}O_2$. Calculated %: H 0.48.

The melting points of the S-benzylpseudothiuronic derivatives of the acids were 148-149° and 141-142°.

4. 2,3,6-Trimethylundecatriene-2,5(6),8-ones-10. Pseudoirones (VII*a* and β). 1) Into an ethereal solution of acid (XIV*a*), prepared by saponification of 3 g (0.012 mole) ester (XIII*a*), was run with energetic stirring 0.6 g (0.027 mole) methyllithium in 30 ml absolute ether. The reaction mass was stirred 45 minutes and poured into iced

water. The ether layer was separated, washed with saturated aqueous sodium thiosulfate and dried with sodium sulfate. The residue after distillation of the solvent was vacuum-distilled; b. p. 123-125° at 3 mm. Yield 1.1 g (53.3%).

d_4^{20} 0.9749, n_D^{20} 1.5326, MR_D 65.73. $C_{14}H_{22}O$ F 3. Calc. 65.46.

Found %: C 81.68; H 11.08. $C_{14}H_{22}O$. Calculated %: C 81.49; H 10.75.

2) Methylmagnesium bromide was prepared from 0.24 g magnesium turnings in 10 ml dry ether by passage of a stream of methyl bromide (2.5 g). To the resultant dark-grey solution was added at 5-10° 1.5 g anhydrous cadmium bromide. The reaction proceeded under gentle boiling of the solvent for 30-45 minutes. The completeness of formation of dimethylcadmium was checked (in a separate test) by the absence of reaction for methylmagnesium bromide with Michler's ketone (emerald-green color). The ether was then distilled off and the residue of the latter was removed by three additions of dry benzene followed by distillation in vacuum. To the residual viscous mass, diluted with 10 ml dry benzene and cooled to 10°, was added with vigorous stirring a benzene solution of 2.26 g acid (XIVβ) chloride. The reaction mass was heated with gentle boiling of the benzene for 1 hour. The cooled solution was decomposed with a little cold water and acidified with 10% sulfuric acid. The aqueous layer was extracted with benzene. The combined extracts were washed with saturated aqueous sodium bicarbonate solution. The residue after removal of the benzene was distilled in vacuum. B. p. 130-131° at 3 mm. Yield 1.5 g (73%).

d_4^{20} 0.9274, n_D^{20} 1.5168, MR_D 66.36. $C_{14}H_{22}O$ F 3. Calc. 65.46.

5. 1,1,3,6-Tetramethyl-2-(buten-2'-one-2")-cyclohexen-(3,4)d,l-α-irone (I). Into 8 g phosphoric acid (d_4^{15} 1.65), cooled to −5°, was added with energetic stirring 2.0 g 2,3,6-trimethylundecatriene-2,5(6),8-one-10 (pseudoirone α or β). The reaction mixture was stirred 20 minutes at 0°, and then 15 minutes at 50-55°; after cooling, the reaction product was run into ice and extracted with ether. The ethereal solution was washed with saturated aqueous sodium bicarbonate solution and dried with sodium sulfate. The residue, obtained after removal of the solvent, was vacuum-distilled. B. p. 118-120° at 2 mm. Yield 1.23 g (61.8%). A light-yellow viscous liquid with a pleasant odor.

d_4^{20} 0.9418, n_D^{20} 1.5143, MR_D 64.42. $C_{14}H_{22}O$ F 2. Calc. 63.73.

Found %: C 81.23; H 10.62. $C_{14}H_{22}O$. Calculated %: C 81.49; H 10.75.

6. 1,1,3,6-Tetramethyl-2-(buten-2'-one-2")-cyclohexen-(2,3)(d,l-β-irones)(II). Into 9 ml sulfuric acid (d_4^{15} 1.83), cooled to −5°, was run with energetic stirring 1.35 g pseudoirone. The mixture was stood at 0° for 10-15 minutes and then poured on to ice and extracted with ether. The ethereal extract was washed with saturated aqueous sodium bicarbonate solution and dried with sodium sulfate. The residue after removal of the ether was distilled in vacuum. B. p. 115-118° at 3 mm.

d_4^{20} 0.9611, n_D^{20} 1.5085, MR_D 63.96. $C_{14}H_{22}O$ F 2. Calc. 63.73.

Found %: C 81.77; H 10.75. $C_{14}H_{22}O$. Calculated %: C 81.49; H 10.75.

7. Ethyl esters of 3'-(1,1,3,6-tetramethylcyclohexen-3,4-yl-2)-propen-2'-oic (1') acids (XVβ and β). Into 18 g phosphoric acid (d_4^{15} 1.65) cooled to −4° was run, with energetic stirring, 6.6 g ethyl ester of 2,3,6-trimethyldecatriene-2,5(6),8-oic-(10) acid. The mixture was stirred 20 minutes at −2°, then 15 minutes at 50°, and the cooled mass was then poured on to ice. The reaction product was extracted with ether, and after removal of the solvent it was distilled in vacuum. B. p. 115-118° at 1.5 mm. Yield 5.35 g (81%).

d_4^{20} 0.9483, n_D^{20} 1.4922, MR_D 72.2. $C_{15}H_{24}O_2$ F 2. Calc. 69.99.

Found %: C 76.15; H 10.23. $C_{15}H_{24}O_2$. Calculated %: C 76.26; H 10.23.

Into 12 ml sulfuric acid (d_4^{15} 1.83) cooled to −5° was run 1.8 g ethyl ester of 2,3,6-trimethyldecatriene-2,6(5),8-oic-(10) acid. The mixture was stirred at 0° for 15 minutes, then for 15 minutes at 50° and poured on to ice. The reaction product was extracted with ether and the residue after distillation of the solvent was distilled in vacuum. B. p. 108-110° at 0.4 mm. Yield 1.42 g (79.9%).

d_4^{20} 0.9766, n_D^{20} 1.4926, MR_D 70.28. $C_{15}H_{24}O_2$ F 2. Calc. 69.99.

8. 3'-(1,1,3,6-Tetramethylcyclohexen-3,4-yl-2)-propen-2'-oic-(1') acid (XVIα). Into sodium ethoxide, prepared from 0.27 g (0.012 g-atom) sodium and 6 ml anhydrous ethanol, was run 0.21 ml (0.012 mole) water and 2.97 g (0.012 mole) ethyl ester of 3'-(1,1,3,6-tetramethylcyclohexen-3,4-yl-2)-propen-2'-oic-(1') acid. The reaction mixture was heated in a stream of nitrogen for 12 hours on a water bath. The resultant sodium salt of acid (XVIα) was dissolved in water and extracted with ether to remove unsaponified ester of (XVα). The reaction mixture was then

acidified with 10% sulfuric acid and extracted with ether. After distillation of the solvent and lengthy standing in a vacuum desiccator, the acid partly crystallized.

Found %: C 74.86, 75.03; H 9.71, 9.79. $C_{13}H_{20}O_2$. Calculated %: C 74.94; H 9.68.

Resolution of the crystalline mixture of diastereoisomeric acids gave, apart from a syrupy acid, a crystalline acid with m. p. 159-164°.

On repetition of the synthesis with large quantities of starting substances and working up of the separated acids with methyllithium [under the conditions for preparation of pseudoirone (VII)], acid (XVIα) gave a mixture of isomeric d,l-α-irones (I) with b. p. 73-78.5° at 0.1 mm and 119-131° at 6 mm.

SUMMARY

1. Two variants of a new synthesis of the isomeric racemic α- and β-irones were realized.

2. The following ethyl esters were isolated and characterized in the course of the synthesis: ethyl esters of 6-hydroxy-2,3,6-trimethyldecadiene-2,8-oic-(10) acid; 2,3,6-trimethyldecatriene-2,5,8-oic-(10) acid; and 2,3,6-trimethyldecatriene-2,6,8-oic-(10) acid.

3. The ethyl ester of 2,3,6-trimethyldecatriene-2,5,8-oic-(10) acid was converted into the diastereoisomeric 3'-(1,1,3,6-tetramethylcyclohexen-3,4-yl-2)-propen-2'-oic-(1') acids and the corresponding α-irones.

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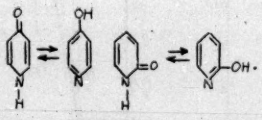
ABSORPTION SPECTRA AND STRUCTURE OF SUBSTITUTED QUINOLINES SERVING AS STARTING SUBSTANCES FOR ANTIMALARIAL AGENTS

III. THE TAUTOMERISM OF 2- AND 4-HYDROXYPYRIDINES

V. I. Bliznyukov and V. M. Reznikov

The chemical structure of 2- and 4-hydroxypyridines has been the subject of numerous investigations. None of the proposed structural formulas, however, satisfactorily describes their properties. These compounds are generally considered to be tautomeric:



I. Absorption spectra of 2- and 4-hydroxypyridines in neutral solutions

Absorption spectra of 2- and 4-hydroxypyridines were first investigated in the ultraviolet region [1]. One absorption band with $\lambda_{max.}$ 3000 A was found for 2-hydroxypyridine, and one with $\lambda_{max.}$ 2560 A for 4-hydroxypyridine. Riegel and Reinhard [2] described the absorption curve of 4-hydroxypyridine in water; their data must be accepted with caution, however, since their preparation was of low purity (m. p. 120° instead of 148°).

Specker and Gawrosch [3] studied the absorption spectra of 2- and 4-hydroxypyridines in methanol and detected two bands for 2-hydroxypyridine at $\lambda_{max.}$ 2970 A and $\lambda_{max.}$ 2270 A, while for 4-hydroxypyridine they found one band with $\lambda_{max.}$ 2560 A.

In some of these studies [1, 3] it was noted that in ethanol solutions 2- and 4-hydroxypyridines and their N-alkyl derivatives possess identical absorption spectra. This suggested the possibility of 2- and 4-hydroxypyridines existing in the ketonic form. However, N-alkylpyridones, assumed to be the "standard" ketonic form, do not possess the chemical properties of unsaturated ketones; thus, for instance, with phosphorus pentachloride they form chloropyridines and with bromine water they form 3,5-dibrom-substituted derivatives; they do not polymerize, do not give colored products in sulfuric acid solutions, possess absorption spectra and molecular refractions different from those of unsaturated ketones, and so forth. In short, the "ketone form" itself is an unusual ketone, possessing special properties.

In the light of the above facts, the study of the structure of 2- and 4-hydroxypyridines can be approached from three independent aspects.

1) Is the proton at the oxygen or the nitrogen (we deliberately do not use the terms "ketonic" or "enolic" forms)?

2) If the proton is at the nitrogen, what is the electronic structure of this unusual "ketone"?

3) Is tautomeric equilibrium involved?

The absorption spectra of 2-hydroxypyridine were examined by us in water, chloroform, ethanol, dioxane, hexane and carbon tetrachloride (Fig. 1, curves 1-6). 2-Hydroxypyridine was studied in water and ethanol in the concentration range of $2 \cdot 10^{-1}$ to $2 \cdot 10^{-4}$ molar, in dioxane and carbon tetrachloride from $2 \cdot 10^{-2}$ to $2 \cdot 10^{-4}$ molar, and in hexane and chloroform from $2 \cdot 10^{-3}$ to $2 \cdot 10^{-4}$ molar.

Only one broad band was found in chloroform, carbon tetrachloride and dioxane with $\lambda_{max.}$ in the 2925-3040 A region, while in water, ethanol and hexane, a second band was found with $\lambda_{max.}$ 2190-2280 A.

The absorption spectra of 4-hydroxypyridine were investigated in ethanol, water, chloroform, dioxane and

benzene (Fig. 1, curves 12-16). 4-Hydroxypyridine was studied in ethanol and water in the concentration range of $2 \cdot 10^{-1}$ to $2 \cdot 10^{-4}$ M, in dioxane from $2 \cdot 10^{-2}$ to $2 \cdot 10^{-4}$ M, in chloroform from $2 \cdot 10^{-3}$ to $2 \cdot 10^{-4}$ M. 4-Hydroxypyridine could not be investigated in hexane and carbon tetrachloride due to the extremely poor solubility (insoluble at a concentration of 10^{-4} M). In all the solvents one band was found with a maximum in the 2520-2570 A region.

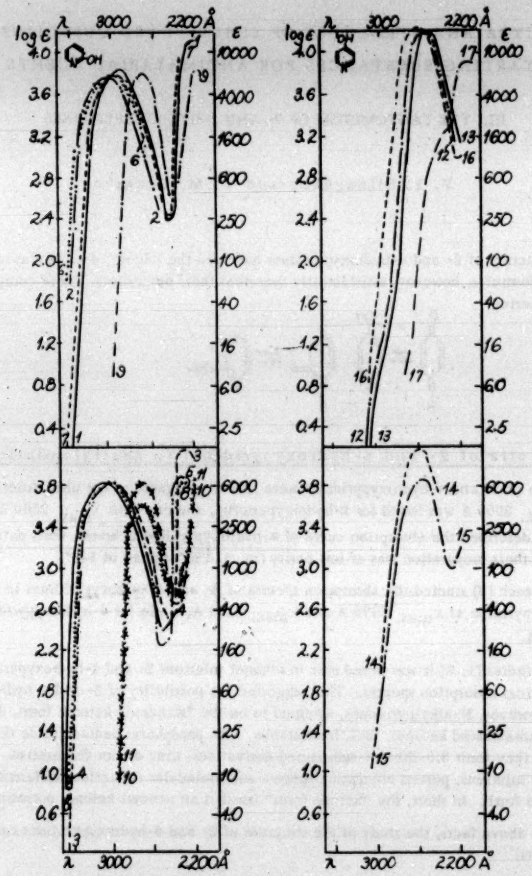
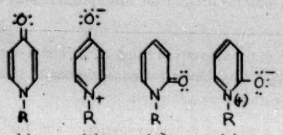


Fig. 1. 2-Hydroxypyridine: 1) in water, 2) in chloroform, 3) in ethanol, 4) in dioxane, 5) in hexane, 6) in carbon tetrachloride; 1-methyl-2-pyridone: 7) in water, 8) in ethanol; 2-ethoxypyridine: 9) in water, 10) in ethanol, 11) in hexane; 4-hydroxypyridine: 12) in ethanol, 13) in water, 14) in chloroform, 15) in dioxane; 1-methyl-4-pyridone: 16) in methanol [3]; 4-methoxypyridine: 17) in methanol [3].

A comparison of the absorption curves of 2- and 4-hydroxypyridines with the absorption curves of the corresponding O-alkyl ethers (Fig. 1, curves 9-11 and 17) and of N-methylpyridones (Fig. 1, curves 7, 8 and 16) shows that in neutral solvents the absorption spectra of 2- and 4-hydroxypyridines possess a great similarity to the spectra of their N-methyl derivatives. The absorption spectra of the ethers, however, are displaced in the direction of shorter waves to the extent of 250-300 A, and they differ considerably in their optical characteristics.

Thus the absorption spectra support the view that actually in all neutral solvents the structure of 2- and 4-hydroxypyridines is similar to that of their N-alkyl derivatives and that, consequently, the proton is located at the ring nitrogen. With such a distribution of atomic nuclei, the electronic configurations may be assumed to be those corresponding to the following structural formulas:



(I) (II) (III) (IV)

where R= H_3CH_3, C_2H_5 etc.

Formulas (I) and (III) correspond to the unsaturated ketone. The absorption spectra in this case must be governed by a conjugated system of double bonds. Formulas (II) and (IV) correspond to a substituted pyridine whose absorption spectra must be governed by interaction of the ring nitrogen with the substituent as in the case of o- or p-hydroxyacetophenone, i. e., it must be a spectrum of the "ortho" or "para" type respectively. Be comparing the curves plotted in Fig. 2 (a and b) we can make a choice between the two formulas under consideration. Fig. 2a contains the curves of the absorption spectra in ethanol of 2-hydroxypyridine and 1-methyl-2-pyridone (curves 1, 2). Also included for comparison are the absorption spectra of 3,5,5-trimethyl-2-cyclohexen-1-one • (curve 4) and o-hydroxyacetophenone (curve 3).

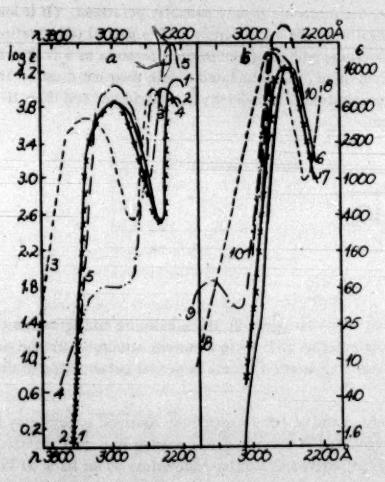


Fig. 2. 1) 2-Hydroxypyridine in ethanol; 2) 1-methyl-2--pyridone in ethanol; 3) o-hydroxyacetophenone in ethanol [6]; 4) 2-aminopyridine in ethylene glycol [7]; 5) 3,5,5-trimethyl--2-cyclohexen-1-one in methanol [4]; 6) 4-hydroxypyridine in ethanol; 7) 1-methyl-4-pyridone in methanol [3]; 8) p--hydroxyacetophenone [6]; 9) phorone in ethanol [5]; 10) 4--aminopyridine in ethylene glycol [7].
Further details in text.

3,5,5-Trimethyl-2-cyclohexen-1-one possesses a spectrum characteristic of a conjugated system: a keto group with a double bond in the ring. The absorption spectrum of o-hydroxyacetophenone is a benzene spectrum of the "ortho type".

The spectra of 2-hydroxypyridine and 1-methyl-2-pyridone contain in the middle ultraviolet two intense, well-developed bands similar to the absorption bands in the spectrum of o-hydroxyacetophenone, i. e., they are spectra of the "ortho type" (Fig. 2a, curves 1, 2, 3). The spectrum of the conjugated system, however, is markedly different (Fig. 2a, curve 4).

In Fig. 2b are plotted the absorption spectra of 4-hydroxypyridine and 1-methyl-4-pyridone (curves 6 and 7) in comparison with the spectra of phorone •• and p-hydroxyacetophenone ••• (curves 8 and 9). The phorone spectrum is characteristic of a conjugated system of crossed double bonds, while that of p-hydroxyacetophenone is a benzene spectrum of the "para type".

Whereas a characteristic of a conjugated system of crossed double bonds is the presence of two bands, one of which is a weak band in the long-wave region and the second a stronger band in the middle ultraviolet (Fig. 2b, curve 9), the spectra of 4-hydroxypyridine and 1-methylpyridone (Fig. 2b, curves 6 and 7), like the

• The absorption spectrum of 3,5,5-trimethyl-2-cyclohexen-1-one is taken from [4].
•• The absorption spectrum of phorone is reproduced from [5].
••• The absorption spectrum of p-hydroxyacetophenone is reproduced from [6].

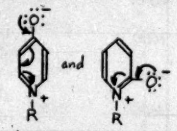
absorption spectrum of p-hydroxyacetophenone, contain only one strong band in the middle ultraviolet which is typical of benzene derivatives with two substituents arranged in the para position (a band of the "para type"). In view of the fact that when analyzing the spectra of hydroxypyridines we took for comparison compounds of the benzene series in which other regularities are possible, we also present the absorption curves of 2- and 4-aminopyridines in ethylene glycol (Fig. 2, curves 5 and 10).

As one of us has shown [7], the main absorption bands of 2- and 4-aminopyridines in ethylene glycol are pyridine bands of the ortho or para types and they are a consequence of interaction of the ring nitrogen with the π-electrons of the pyridine ring and with the amino group.

A comparison of the absorption curves of 2-hydroxypyridine and 1-methyl-2-pyridone in ethanol with the absorption curve of 2-aminopyridine in ethylene glycol (Fig. 2, curves 1, 2 and 5), as well as a comparison of the absorption curves of 4-hydroxypyridine and 1-methyl-4-pyridone in ethanol, with the absorption curve of 4-aminopyridine in ethylene glycol (Fig. 2, curves 6, 7 and 10) reveals a very close similarity.

Thus, from an inspection of the absorption spectra we see that the ring nitrogen in the molecule of 2- and 4--hydroxypyridines is an electron-acceptor, whereas the oxygen is an electron-donating atom; between them and the ring is established an interaction of the π-conjugated type, which is reflected in the spectrum by the development of intense "ortho" and "para" absorption bands. In the light of these facts we ought to accept for 2- and 4-hydroxypyridines the formulas corresponding to the hydroxypyridine structure, rejecting the formulas of an unsaturated ketone.

It must be noted that comparison of the absorption spectra of 2- and 4-hydroxypyridines with the spectra of the corresponding aminopyridines reveals a 3 1/2 - 4 times lower intensity of the "ortho" and "para" absorption bands of 2- and 4-hydroxypyridines in comparison with the corresponding bands of the aminopyridines. This supports the view that the oxygen carries a partial (δ-) negative charge, i. e. the molecule is only partially polarized. (It is known that the negatively charged phenolic oxygen is optically similar to the amino group.) The partial polarization of the molecule is confirmed by the lower dipole moment of 4-hydroxypyridine, given in the literature as 6 D [8]. If, however, the intraionoid formula (II) is accepted for 4-hydroxypyridine, the calculated dipole moment must be 19.9 D. Analysis of the chemical, physico-chemical and optical properties of 2- and 4-hydroxypyridines and their N-alkyl derivatives allows us to propose structural formulas for them:



that reflect the following features: 1) the proton is located at the nitrogen; 2) the electronic configuration of 2- and 4-hydroxypyridines and of N-alkylpyridones corresponds to a pyridine and not to a ketonic structure; 3) the ring nitrogen is an electron-accepting and the oxygen an electron-donating atom; 4) there is partial polarization of the molecule.

Depending upon the reaction conditions (type of medium and of active agent) the electron system may be deformed with formation of a reaction center both at the oxygen and at the nitrogen, resulting in a dual reactivity of 2- and 4-hydroxypyridones. It should be noted that Auwers [9] arrived at similar conclusions as far back as 1930 on the basis of spectrochemical investigations.

The absorption spectra of 2- and 4-hydroxypyridines were studied in a large number of neutral solvents with the objective of detecting the two hypothetical tautomeric forms. If marked shifting of the tautomeric equilibrium had occurred in this case, we might have expected to find a shift in one direction or another with change in the polarity of the solvent. Such an effect could not be detected, however, in the ultraviolet spectra. In all neutral solvents the character of the absorption spectra of 2- and 4-hydroxypyridines remains unchanged.

II. Absorption spectra of 2- and 4-hydroxypyridines in acids

The absorption spectra of 2- and 4-hydroxypyridines in ethanol solution of hydrochloric acid were first investigated by Becker and Baly [1]. They found one band with $\lambda_{max.}$ 2850 A in the case of 2-hydroxypyridine hydrochloride, and one weak band with $\lambda_{max.}$ 3225 A and a second very strong band with $\lambda_{max.}$ 2325 A in the case of the 4-hydroxypyridine salt.

Only one band with a maximum at λ 2350 A was found on examining 4-hydroxypyridine in 0.1 M ethanol solution of hydrochloric acid. Finally, Adams [10] in an examination of the structure of leucenol incidentally gives a small portion of the curve of 2-hydroxypyridine in 0.1 M methanol solution of hydrochloric acid with a maximum at λ 2800 A.

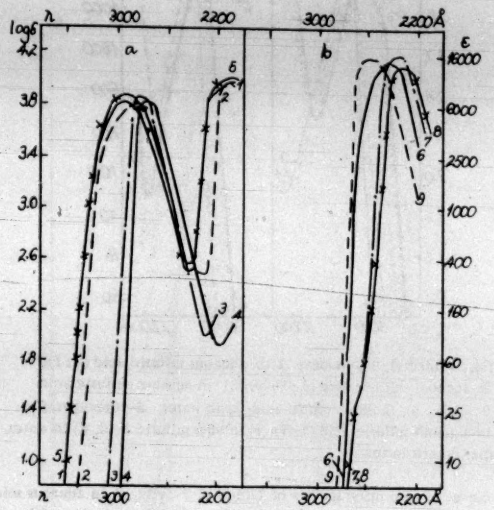


Fig. 3. 2-Hydroxypyridine: 1) in aqueous sulfuric acid solution (1 : 1); 2) in aqueous sulfuric acid solution (1 : 100); 3) in aqueous sulfuric acid solution (1 : 25,000); 4) in 98% sulfuric acid; 5) in water. 4-Hydroxypyridine: 6) in aqueous sulfuric acid solution (1 : 1); 7) in aqueous sulfuric acid solution (1 : 2); 8) in 98% sulfuric acid; 9) in water. Further details in text.

We made a detailed study of 2- and 4-hydroxypyridines in aqueous solutions of sulfuric acid of various concentrations and in concentrated sulfuric acid. In view of the fact that the absorption spectra of 4-hydroxypyridine in hydrochloric acid solution reported in the literature [1, 3] are contradictory, we subjected the compound to thorough purification. Spectrographic investigation of this preparation in solutions of sulfuric acid revealed one very strong absorption band; the weak band with $\lambda_{max.}$ 3225 A was not detected; this agrees with the literature [3]. Incidentally an investigation was made in sulfuric acid solutions of the absorption spectra of 2-ethoxypyridine and 1-methyl-2-pyridone. In Fig. 3a are presented the absorption spectra of 2-hydroxypyridine in sulfuric acid of various concentrations. All the spectra were plotted in the concentration range of $2 \cdot 10^{-2}$ to $2 \cdot 10^{-4}$ M. With ratios of 1 and 10 M sulfuric acid to 1 mole 2-hydroxypyridine (curve 1) its absorption spectrum remains unchanged; this is also true of aqueous solutions (the absorption curve at a 1 : 10 M ratio is omitted to save space). At ratios of 1 : 100 and 1 : 1000 M sulfuric acid to 1 mole substance (curve 2) the absorption curve is displaced in the direction of shorter waves to the extent of 100-120 A; however, the character of the curve as a whole does not change (the absorption curve at a ratio of 1 : 100 M is omitted). Addition of 25,000 M sulfuric acid per mole of hydroxypyridine (curve 3) leads to a further shift of the curve toward the ultraviolet. The band becomes narrower and the minimum is lowered by a factor of 4. Finally, in concentrated sulfuric acid (curve 4) the curve is shifted still further into the ultraviolet.

Fig. 3b shows the absorption spectra of 4-hydroxypyridine in sulfuric acid of various concentrations. All the curves were plotted in the concentration range of $2 \cdot 10^{-2}$ to $2 \cdot 10^{-4}$ M. Addition of 0.5 M sulfuric acid to 1 mole 4-hydroxypyridine has no effect whatever upon its spectrum (the curve is not included in Fig. 3). On addition, however, of 1 M sulfuric acid (Fig. 3b, curve 6) the absorption curve is displaced in the direction of shorter waves; addition of 2 M sulfuric acid causes a further sharp displacement in the same direction (curve 7). 10 M sulfuric acid (curve not given) and even 98% sulfuric acid (curve 8) did not result in further marked changes in the absorption spectrum of 4-hydroxypyridine.

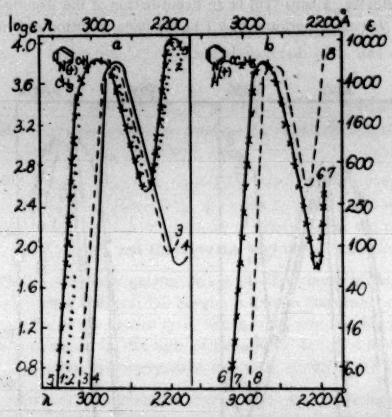


Fig. 4. 1-Methyl-2-pyridone: 1) in aqueous sulfuric acid (1:1); 2) in aqueous sulfuric acid (1:1000); 3) in aqueous sulfuric acid (1:25,000); 4) in 98% sulfuric acid; 5) in water. 2-ethoxypyridine: 6) in aqueous sulfuric acid (1:1); 7) in 98% sulfuric acid; 8) in water. Further details in text.

Fig. 4a contains the curves of absorption spectra of 1-methyl-2-pyridone in aqueous solutions of sulfuric acid (at molar ratios of substance to sulfuric acid of 1:1, 1:1000 and 1:25,000) and in concentrated sulfuric acid. Addition of 1 M sulfuric acid per mole substance (curve 1) has no influence upon the absorption spectrum of 1-methyl-2--pyridone. Addition of 1000 M sulfuric acid (curve 2) leads to a slight displacement of the absorption curve toward the ultraviolet. On addition, however, of 25,000 M sulfuric acid the absorption band becomes narrower, the minimum is lowered by a factor of 4, and the whole of the curve is hypsochromically displaced to the extent of 200 A (Fig. 4a, curve 3). In concentrated sulfuric acid (curve 4) the curve is shifted still a little further into the ultraviolet.

Fig. 4b contains the curves of the absorption spectra of 2-ethoxypyridine in dilute sulfuric acid (substance/sulfuric acid molar ratio of 1:1) and in concentrated sulfuric acid (Fig. 4b, curves 6 and 7). At 1:1 ratio is observed bathochromic displacement of the absorption curve of 2-ethoxypyridine by 100 A in comparison with the absorption curve in water (Fig. 4b, curves 6 and 8); at the same time the band narrows and the minimum is lowered by a factor of nearly 6. In concentrated sulfuric acid (Fig. 4b, curve 7) the character of the absorption does not change further when compared with the absorption in dilute sulfuric acid.

The curves of absorption spectra represented in Figs. 3 and 4 permit us to reach the following conclusions: a) in aqueous solutions of sulfuric acid the absorption spectra of 2-hydroxypyridine, 4-hydroxypyridine and 1-methyl-2--pyridone undergo a hypsochromic shift to the extent of 200 A, while the absorption spectrum of 2-ethoxypyridine is bathochromically displaced by 100 A; b) the changes observed in the absorption spectra of 2-hydroxypyridine with changing ratio of substance to sulfuric acid are repeated with exceptional uniformity in the spectra of 1-methyl-2--pyridone; c) it follows from a comparison of the absorption spectra of 2-hydroxypyridine and 4-hydroxypyridine that whereas in 1:1 ratio in the case of 4-hydroxypyridine the absorption maximum is shifted toward the ultraviolet, and in 1:2 ratio the effect is the same as with concentrated sulfuric acid, in the case of 2-hydroxypyridine both 1 M and 1000 M sulfuric acid have an insignificant effect upon the absorption spectrum, and only with 25,000 M sulfuric acid per mole of 2-hydroxypyridine is an effect similar to that of concentrated sulfuric acid exerted; d) the curves of the absorption spectra in dilute sulfuric acid of 2-hydroxypyridine (1:1000 ratio, Fig. 3, curve 2), 1-methyl-2-pyridone (1:1000 ratio, Fig. 4, curve 2) and 4-hydroxypyridine (1:1 ratio, Fig. 3, curve 6) contain a break which is caused by dilution of the solutions in passing from one concentration to another. The cause of this break is the hydrolysis of the pyridine salts formed in solution.

In Fig. 5 are represented the absorption spectra of 2- and 4-hydroxypyridones in comparison with the corresponding absorption curves of their O- and N-alkyl derivatives. The absorption of all three types of compounds in acids is

seen to be completely identical (curves 1, 2, 3 and 7, 8, 9). Under the action of acids the spectrum of the O-derivatives is bathochromically displaced (Fig. 5, curves 6, 2 and 12, 9), whereas the curves of 2- and 4-hydroxypyridines and their N-derivatives are displaced in the direction of shorter waves (curves 4, 6, 1, 3 and 10, 11, 7, 8). All the displacements of the curves of the compounds in question are considered in relation to absorption in ethanol solution.

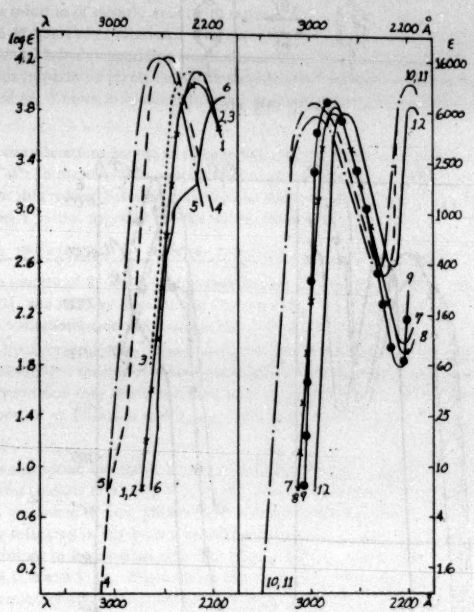
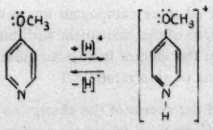
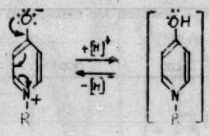


Fig. 5. 1) 4-hydroxypyridine in 98% sulfuric acid, 2) 4-methoxypyridine in 0.1 M methanol solution of HCl [3], 3) 1-methyl-4-pyridone in 0.1 M methanol solution of HCl [3], 4) 4-hydroxypyridine in ethanol, 5) 1-methyl-4-pyridone in methanol [3], 6) 4-methoxypyridine in methanol [3], 7) 2-hydroxypyridine in aqueous H_2SO_4 (1:25,000), 8) 1-methyl-2-pyridone in aqueous H_2SO_4 (1:25,000), 9) 2-ethoxypyridine in aqueous H_2SO_4 (1:2), 10) 2-hydroxypyridine in water, 11) 1-methyl-2--pyridone in water, 12) 2-ethoxypyridine in water.

The bathochromic displacement of the curve of the absorption spectrum of 4-methoxypyridine indicates that salt formation takes place at the ring nitrogen, and that apparently the character of the absorption is determined by absorption of the "methoxypyridinium" cation.



The displacement of the absorption curves of 4-hydroxypyridine and 1-methyl-4-pyridone toward the shorter wave region indicates that addition of acid causes addition of proton not to nitrogen but to oxygen, as was correctly suggested previously [11, 12], and which was to be expected in agreement with our proposed structural formulas.



R = H, CH_3, etc.

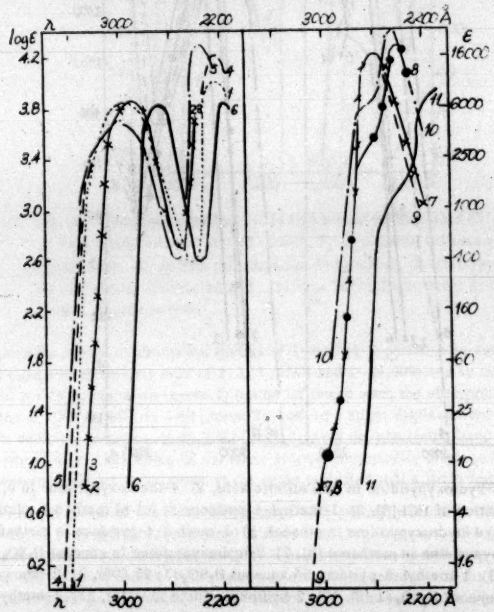


Fig. 6. 2-Hydroxypyridine: 1) in C_2H_5ONa (1:1), 2) in C_2H_5ONa (1:10), 3) in 2 M C_2H_5ONa solution, 4) in ethanol; 2-aminopyridine: 5) in ethanol [7]; 2-ethoxypyridine: 6) in ethanol; 4-hydroxypyridine: 7) in C_2H_5ONa (1:1), 8) in 2 M solution of C_2H_5ONa, 9) in ethanol; 4-aminopyridine: 10) in ethanol [7]; 4-methoxypyridine: 11) in methanol [3].

Consequently, the absorption of all three compounds was governed by one and the same "pyridinium" cation in which the essential feature is interaction of the substituent with the π-electrons of the ring and the positively charged ring nitrogen. Hence the similarity of the spectra in an acid medium. (A similar interpretation can be put upon the absorption spectra of 2-hydroxypyridine in acid solutions.)

The anomalous displacement of the curves of the absorption spectra of 2- and 4-hydroxypyridines under the action of acids and alkalies was one of the most important arguments in support of their tautomerism. Above we gave an explanation of this phenomenon without resorting to the concept of tautomerism; for greater certainty, however, we made a closer study of the problem of tautomerism. It is known that tautomeric transformations are realized even under the catalytic action of hydrogen or hydroxyl ions and take place over a period of time. We therefore studied the absorption spectra of 4-hydroxypyridine in presence of 0.1 M sulfuric acid and 0.5 M sulfuric acid per mole of 4-hydroxypyridine. Such small amounts of acid caused no changes at all in the spectrum of 4-hydroxypyridine; it remained the

same as in water (for this reason the absorption curves are not included in Fig. 3b); only with a 1:1 ratio of 4-hydroxypyridine to sulfuric acid are any changes observed in its spectrum (Fig. 3b, curve 6). This change is an indication of the start of salt formation at the negatively charged oxygen.

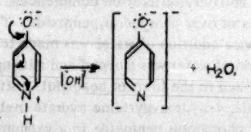
We next checked the influence of the time factor. The absorption spectra of 4-hydroxypyridine were investigated in aqueous solution of sulfuric acid (with ratios of 0.1 and 0.5 M sulfuric acid per 1 mole 4-hydroxypyridine 24 hours and 48 hours after dilution). The absorption spectra remained unchanged – the same as in water. A similar investigation of 2-hydroxypyridine was not undertaken because an inspection of the curves in Fig. 3a indicates that 2-hydroxypiperidine reacts only with considerable amounts of sulfuric acid (100 M and more of concentrated sulfuric acid per 1 mole 2-hydroxypyridine), and consequently a catalytic action of the acid is here excluded.

The foregoing considerations permit us to conclude that the interaction of hydroxypyridines with acids is the usual reaction of salt formation. The special feature of this reaction is that the attack by the proton takes place not at the nitrogen, as might have been expected and as was assumed by Becker and Baly [1], but at the oxygen, since the oxygen bears a partial negative charge and is, consequently, the most basic part of the molecule.

III. Absorption spectra of 2- and 4-hydroxypyridines in sodium ethoxide solutions

The absorption spectra of 2- and 4-hydroxypyridines in an alkaline medium were studied for the first time by Becker and Baly [1], and later by Specker and Gawrosch [3]. The former qualitatively examined 2- and 4-hydroxypyridines in sodiumethoxide and found in the case of 2-hydroxypyridine one band with $\lambda_{max.}$ 2940 A and in the case of 4-hydroxypyridine two bands characterized by inflexions with $\lambda_{max.}$ 2770 A and 2440 A. The latter described the absorption spectra of these compounds in 0.01 and 0.1 M solutions of sodium methoxide. In the case of 2-hydroxypyridine they found one band with $\lambda_{max.}$ 2940 A, and in the case of 4-hydroxypyridine two bands – one in the form of an inflexion with $\lambda_{max.}$ 2640 A and the second as a well-developed band with $\lambda_{max.}$ 2400 A.

We studied the absorption spectra of 2- and 4-hydroxypyridines in sodium ethoxide solutions at substance/sodium ethoxide ratios (molar) of 1:0.1; 1:1; 1:100, also in 2 M sodium ethoxide solution. In alkaline solutions the hydroxypyridines are bound to form phenoxides. Whereas, however, in the case of phenols the formation of phenoxides is usually reflected in the spectra by displacement of the curve to the long-wave side, in the case of 2- and 4-hydroxypyridines in 2 M sodium ethoxide solution the absorption curve is shifted into the region of shorter waves (Fig. 6, curves 1, 3 and 9, 8). The cause of this anomalous displacement of the absorption curves of hydroxypyridines under the action of alkalies has not hitherto been established. This fact finds a natural explanation in our proposed formula for the structure of 2- and 4-hydroxypyridines. A reaction according to the following scheme takes place between 2- and 4-hydroxypyridines and caustic alkalies:



As indicated above, in the case of pyridine derivatives the addition of a proton at the ring nitrogen is accompanied by a bathochromic shift of the absorption curve. In an alkaline medium salt formation takes place with cleavage of a proton from the ring nitrogen, and the curve of the absorption spectrum is naturally shifted toward the short-wave region of the spectrum.

The phenolic structure of 2- and 4-hydroxypyridines in an alkaline medium is also confirmed by a comparison of their absorption spectra with those of the corresponding aminopyridines, since we know from the literature that the amino group is optically similar to the phenolate ion [13].

In Fig. 6 (curves 5 and 10) are shown the absorption spectra of 2- and 4-aminopyridines in ethanol and of 2- and 4-hydroxypyridines (curves 3 and 8) in sodium ethoxide. Comparison of these absorption curves reveals the great similarity both in the general character of the curves and in the position and intensity of the absorption bands.

Thus the chemical evidence for the phenolic structure of the sodium salts of 2- and 4-hydroxypyridines is confirmed by the ultraviolet absorption spectra. Concerning, however, the tautomerism of 2- and 4-hydroxypyridines in an alkaline medium, an inspection of the curves in Fig. 6 reveals that a change in the absorption spectra of hydroxypyridines under the action of sodium ethoxide is only observed at a hydroxypyridine/sodium ethoxide

ratio of 1 : 100 (Fig. 6, curves 2, 3). Lower concentrations of sodium ethoxide were ineffective, and it is therefore impossible to speak of a catalytic action of the alkali ions.

Furthermore, we investigated the absorption spectra of 2- and 4-hydroxypyridines at hydroxypyridine/sodium ethoxide ratios of 1 : 0.1 and 1 : 1 at intervals of 1, 2 and 5 days after preparation of the solution. A change in the absorption spectra over a period of time was not detected (the absorption curves are not given in Fig. 6 because they are identical with the absorption curves in ethanol).

Consequently the most important factors that are characteristic of tautomeric transformations – the catalytic action of alkali ions and the occurrence of a rate process – are lacking.

EXPERIMENTAL

2-Hydroxypyridine was prepared by diazotization of 2-aminopyridine [14]. The sodium salt was then isolated and recrystallized from alcohol; it was then decomposed with carbon dioxide in alcohol solution. After separation of the precipitate, the mother liquor was evaporated down until crystallization commenced. The product was twice recrystallized from benzene. Colorless needles with m. p. 107°.

2-Ethoxypyridine was obtained by the action of ethyl iodide upon the silver salt of 2-hydroxypyridine [15]. The preparation was purified by distillation. After two distillations a middle cut was collected with b. p. 158-159°. According to [15] the b. p. is 155-156°.

1-Methyl-2-pyridone was obtained by oxidation of pyridine methiodide with potassium ferricyanide [16]. It was purified by distillation. After two distillations in vacuum a heart fraction was collected with b. p. 121° (10 mm). According to [17] the b. p. is 121° (10 mm). A freshly distilled preparation was used each time for spectrographic investigation.

4-Hydroxypyridine was obtained by decarboxylation of chelidamic acid [18]. When purified [19] by distillation in vacuum followed by boiling in benzene, a band with $\lambda_{max.}$ 2880 A and ϵ 28 was got in spite of the good melting point, although this band was absent from the spectra of 4-hydroxypyridine described by Specker and Gawrosch. For this reason we developed a more thorough method of purification of 4-hydroxypyridine.

The 4-hydroxypyridine obtained after decarboxylation was dissolved in water and the solution digested with active carbon for 15 minutes. The carbon was separated and the colorless filtrate evaporated and neutralized with caustic alkali. To the solution of the sodium salt of 4-hydroxypyridine was added 50% sodium hydroxide in large excess until the sodium salt of 4-hydroxypyridine started to crystallize. After 24 hours the crystalline precipitate was filtered on a linen filter, dried, and recrystallized from alcohol. The recrystallized sodium salt of 4-hydroxypyridine was dissolved in alcohol and decomposed with carbon dioxide. The precipitate was separated by filtration and the mother liquor concentrated until crystallization commenced. The obtained hydrate of 4-hydroxypyridine was dehydrated in a vacuum-desiccator over phosphorus pentoxide. The anhydrous 4-hydroxypyridine was dissolved in chloroform by heating, and dropwise addition of water was made to the solution with good stirring until turbidity developed. At this point the addition of water was stopped and stirring continued until crystallization commenced. 4-Hydroxypyridine hydrate crystallized in the form of beautiful, lustrous, strongly refracting plates. After freeing from chloroform and drying in the air, 4-hydroxypyridine hydrate melted at 67°. Anhydrous 4-hydroxypyridine was obtained by drying the hydrate over phosphorus pentoxide in a vacuum-desiccator. It formed a colorless powder m. p. 148°. The literature [19] also gives 148°. 4-Hydroxypyridine purified in this way did not give a weak band at $\lambda_{max.}$ 2880 A.

SUMMARY

1. A study was made of the absorption spectra in the ultraviolet of 2- and 4-hydroxypyridines, 1-methyl-2-pyridone and 2-ethoxypyridine in neutral solvents, sulfuric acid of various concentrations and sodium ethoxide of various concentrations.

2. It was established that the absorption spectra of 2- and 4-hydroxypyridines in neutral solvents are identical with the spectra of their N-alkyl derivatives and are also similar to the spectra of ortho- and para-disubstituted benzenes.

3. A formula is advanced for the electronic structure of 2- and 4-hydroxypyridines and their N-alkyl derivatives.

4. It was found that 2- and 4-hydroxypyridines form salt at the oxygen atom both with acids and with caustic alkalies; 2-hydroxypyridine reacts with acids at higher acid concentrations than does 4-hydroxypyridine.

5. Tautomerism was not observed in the spectra of 2- and 4-hydroxypyridines.

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THE PROBLEM OF THE NATURE OF THE PRIMARY PRODUCTS OF REACTION OF AMINES WITH NITROUS ACID

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The problem of the nature of the primary products of interaction of amines with nitrous acid is of outstanding importance for clarification of the mechanism of the diazotization reaction. Following Bamberger [1], a number of investigators have assumed one of the stages of this reaction to be the formation of various products of addition of molecules of diazotizing agent to molecules of amines.

In a series of papers by Earl and co-workers [5] on the products of reaction of hydrochlorides of primary and secondary amines with sodium nitrite in the absence of free acid, the possibility is assumed of regarding the primary reaction of diazotization and nitrosation as the simple addition of free amine to the undissociated nitrous acid according to the equation: $HO-N=O + NHR_2 \longrightarrow (HO)_2N-NR_2$, i. e., the structure of N-dihydroxyhydrazines is attributed to the primary products of reaction of amines with nitrous acid. In a previously mentioned paper [4] L. V. Grachev identifies these products with amine-nitrites, although Earl himself does not do so.

It appeared to us of interest to check the correctness of this identification, particularly since it is not perfectly clear from Earl's papers what relation the amine-nitrites bear to the primary products of reaction of amines with nitrous acid, i. e., to the N-dihydroxyhydrazines.

All the amine-nitrites studied by Earl were extremely unstable; they decomposed in the air even at temperatures below 0°. Earl studied them exclusively by physico- chemical methods (dilatometry, etc.). In an attempt to obtain stable derivatives of these substances, we subjected aniline nitrite, prepared by Earl's method, to reaction with diazomethane; copious evolution of gas at once resulted and a dark, oily liquid was formed which distilled in vacuum without decomposition. The prepared substance could not be the dimethoxy derivative $C_6H_5NH-N(OCH_3)_2$, since not more than 1 mole diazomethane was consumed per mole aniline nitrite during its formation. Nor could it be the diazo ether $C_6H_5N=NOCH_3$, since it did not contain methoxyl groups [6]. Molecular weight determination showed that the investigated substance was not a product of polymerization, and led to the hypothesis that it was aniline. This was confirmed.

Assigning arbitrarily the formula $C_6H_5NH_2 \cdot HNO_2$ to aniline nitrite, the reaction with diazomethane can be imagined to proceed as follows:

$$C_6H_5NH_2 \cdot HNO_2 + CH_2N_2 \longrightarrow C_6H_5NH_2 + N_2 + CH_3ONO.$$

In that event methyl nitrite should be present in the gaseous products of reaction. Its presence was established by qualitative reactions [8], and later a quantitative determination was performed [9]. Methyl nitrite was found in 75.5% of the amount that would have separated if the reaction of formation of aniline nitrite from aniline hydrochloride had gone quantitatively. Bearing in mind that aniline nitrite starts to decompose in the very instant of formation even at temperatures below 0°, we must conclude that the amount of methyl nitrite evolved approximately corresponds to the amount of aniline nitrite taken.

The observations on aniline nitrite were extended to analogous substances prepared from o-, m- and p-toluidines, α-naphthylamine and monoethylaniline. In all cases the corresponding amine nitrites instantaneously broke down under the action of diazomethane with formation of the original amine and methyl nitrite. The latter was quantitatively determined. Yields of methyl nitrite are set forth in Table 1.

The facility with which amine nitrites break down under the action of diazomethane in a neutral medium and the character of the resultant products are inconsistent with the hypothesis that they might be the N-dihydroxyhydrazines. The assumption that diazomethane can instantaneously decompose compounds of the type $RNH-N(OH)_2$ and $RR'N-N(OH)_2$, which are characterized by the presence of a covalent bond between the nitrogen atoms, appears to us highly improbable. It is known that in compounds of both the aromatic and the aliphatic series with a

covalent bond between the nitrogen atoms (nitramines $RNHNO_2$, hydrazines $RNHNH_2$, hydrazo compounds RNHNHR, etc.) the bond is quite stable, and there are no grounds for regarding it as unstable to the action of diazomethane in a neutral medium in compounds of the type of the N-dihydroxyhydrazines. It is more reasonable to assume, as Earl assumed, that the so-called amine nitrites are nitrous acid salts of the corresponding amines, i. e., they have the structure $RNH_2 \cdot HNO_2$ or $[\overset{+}{R}NH_3](NO_2)^-$ in the case of primary amines and $RR'NH \cdot HNO_2$ or $[\overset{+}{R}R'NH_2](NO_2)^-$ in the case of secondary amines. This assumption explains the facility with which amine nitrites react with diazomethane to form the free amine and methyl nitrite: the amine salt does not contain a covalent bond between the nitrogen atoms, and the anion of nitrous acid can interact with diazomethane with the velocity of ionic processes:

$$[\overset{+}{R}NH_3](NO_2)^- + CH_2N_2 \longrightarrow RNH_2 + CH_3ONO + N_2.$$

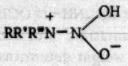
TABLE 1

Nitrite	Methyl nitrite evolved (in %)
Aniline	75.5
o-Toluidine	88.1
m-Toluidine	59.5
p-Toluidine	48.7
α-Naphthylamine	64.0
Monoethylaniline	96.5

TABLE 2

Nitrite	Methyl nitrite found		Melting point of derivatives	
	(g)	(%)	Found	Literature data [7]
o-Toluidine	0.749	88.1	108°	110°
m-Toluidine	0.437	59.5	113	114
p-Toluidine	0.414	48.7	116	118
α-Naphthylamine	0.435	64.0	157	157
Ethylaniline	0.749	96.5	88	88
Diethylaniline	0.607	92.0	140	142

The indicated structure of amine nitrates assumes the existence of corresponding derivatives of tertiary amines, $RR'R''N \cdot HNO_2$ or $[\overset{+}{R}R'R''NH](NO_2)^-$; it is extremely strange that in Earl's papers there are no indications of the possibility of formation of nitrites of tertiary amines. If I. V. Grachev is correct in identifying amine nitrites with N-dihydroxyhydrazines, then their formation from tertiary amines must be regarded as impossilbe, since in that event we should obtain the extremely improbable internally ionized compounds of the type of



Experiments with diethylaniline gave positive results. Reaction of diethylaniline hydrochloride with sodium nitrite gave diethylaniline nitrite, treatment of which with diazomethane immediately led to reaction with formation of methyl nitrite in 92% yield and diethylaniline.

Experiments on the reaction of diazomethane with N- and C-nitroso compounds gave negative results. Under conditions similar to the conditions of interaction with amine nitrites, neither N-nitrosoethylaniline nor p-nitrosodiethylaniline entered into reaction with diazomethane, and gaseous products were not formed. Hence it follows that methyl nitrite is the result of reaction of diazomethane with the primary product of interaction of amines with nitrous acid, i. e., with the nitrous acid salt of the amine ("amine nitrite"), and not with the products of more far-reaching processes such as nitroso compounds.

It is interesting to note that the attempt to obtain p-nitrosodiethylaniline nitrite by the action of nitrite on p-nitrosodiethylaniline hydrochloride did not meet with success: there was violent evolution of oxides of nitrogen accompanied by considerable development of heat, and the formation of amine nitrite was not observed. Evidently the nitroso group in the p-position so lowers the basicity of diethylaniline that the formation of a salt of a weak acid such as nitrous acid becomes impossible.

EXPERIMENTAL

Preparation of aniline nitrite and its reaction with diazomethane. To a mixture of 20 ml ether and a solution of 1.5 g $NaNO_2$ in 3 ml water, cooled to −18°, was added a solution (cooled to −10°) of 2 g aniline hydrochloride in 5 ml water. (The aniline hydrochloride had previously been washed with ether and dried.) The resultant white, clotty precipitate of aniline nitrite was brought into ethereal solution by vigorous shaking. The ether layer was separated from the aqueous layer; the latter was washed with a little ether and the two ethereal solutions were combined.

To the solution, cooled to −15°, was gradually added a solution of diazomethane prepared from 2.5 g nitrosomethylurea (by the action of 10 ml 40% KOH at −5° in presence of 30 ml ether followed by washing of the aqueous layer with ether; the total volume of ethereal solution was 35 ml). Violent evolution of gas commenced immediately. Diazomethane was introduced until gas ceased to come off. 17 ml of the ethereal solution of diazomethane was used out of the total of 35 ml (consumption of diazomethane 0.495 g, i. e., about 0.76 mole per 1 mole aniline nitrite). The ether was evaporated to leave a dark, oily liquid soluble in ether, alcohol, benzene and HCl solution, insoluble in NaOH solution. It distilled without decomposition in vacuum [52° (4 mm), 73° (10 mm)]. It gave a violet coloration with calcium hypochlorite solution. After reaction with sodium nitrite in hydrochloric acid solution it reacted with an alkaline solution of β-naphthol with formation of an orange substance.

Found %: OCH_3 0 $C_6H_5NHN(OCH_3)_2$. Calculated %: OCH_3 36.9. $C_6H_5N{=}NOCH_3$. Calculated %: OCH_3 22.8. Found M: 97.1. $C_6H_5NH_2$. Calculated M: 93.

Melting point of p-toluenesulfo derivative 103° (from alcohol). A mixed test with p-toluenesulfoanilide [7] did not give a depression of melting point.

The gaseous substances evolved on reaction of aniline nitrite with diazomethane were passed through a solution of sulfanilic acid; the latter acquired a markedly different red-violet color. Passage of the gaseous products through an acetic acid solution of α-naphthylamine, a yellow-orange suspension was formed. In both cases the action of the gaseous products led to results qualitatively identical [8] with those of the action of specially prepared methyl nitrite [10].

Quantitative determination of methyl nitrite. An ethereal solution of aniline nitrite, prepared from 2 g aniline hydrochloride, was put into a flask cooled externally with ice, and through a dropping funnel was gradually introduced an ethereal solution of diazomethane. The evolved gases were entrained in a stream of CO_2 (from a Kipps apparatus connected to the flask) and passed via a wash bottle containing saturated sodium bicarbonate solution into a system of 4 absorbers (bulb type) and 3 wash bottles filled with acidified potassium iodide solution 16 g KI in 120 ml water and 40 ml HCl (s. g. 1.19) in 2 wash bottles and bulb-absorbers and 2 g KI in 40 ml water acidified with a few drops HCl in the last (check) wash bottle]. The system was closed by a beaker containing water. The air was purged out of the whole system with CO_2 before introduction of the ethereal solution of aniline nitrite into the reaction flask.

The diazomethane solution was introduced over a period of about 30 minutes, after which the CO_2 stream was passed for 2 hours for final displacement of the methyl nitrite formed into the absorption bottles. The content of the absorption vessels was transferred to a measuring cylinder and the iodine released was titrated with thiosulfate solution in presence of starch. Found CH_3ONO 0.71 g, calculated for aniline nitrite from 2 g aniline hydrochloride 0.94 g CH_3ONO. Yield of methyl nitrite 75.5%.

Preparation of other amine nitrites and their reaction with diazomethane. The amine nitrites from o-, m- and p-toluidine, α-naphthylamine, and mono- and diethylanilines were prepared by exactly the same method as for aniline nitrite, starting from 2 g of the amine. Reaction with diazomethane and determination of the methyl nitrite were accomplished as described above. The experimental data appear in Table 2. The yields of methyl nitrite are given in percentages of those theoretically possible in quantitative formation and assuming absolute stability of the amine nitrites. The amines resulting from reaction of amine nitrites with diazomethane were identified in the form of the p-toluenesulfo derivatives, with exception of diethylaniline which was identified as the picrate.

Reaction of diazomethane with N-nitrosoethylaniline. N-Nitrosoethylaniline, prepared according to [11], cooled to −5°, was treated with an ethereal solution of diazomethane in the apparatus for determination of methyl nitrite. Evolution of gas and darkening of the potassium iodide solution were not observed.

Reaction of diazomethane with p-nitrosodiethylaniline. An ethereal solution of p-nitrosodiethylaniline (prepared as in [12]), cooled to −5°, was treated with an ethereal solution of diazomethane in the apparatus for determination of methyl nitrite. Evolution of gas and darkening of the potassium iodide solution were not observed.

Reaction of p-nitrosodiethylaniline with nitrous acid. Into a solution (cooled to −15°) of p-nitrosodiethylaniline hydrochloride was run a solution (cooled to −15°) of $NaNO_2$. An energetic reaction commenced immediately and was accompanied by evolution of brown gaseous products (oxides of nitrogen) and by marked heat development. Formation of a precipitate of amine nitrite was not observed.

We express our sincere gratitude to N. N. Vorozhtsov for valuable advice and constant help in the investigation.

SUMMARY

1. A study was made of the reaction of diazomethane with amine nitrites prepared by the action of sodium nitrite on the hydrochlorides of aniline, o-, m- and p-toluidines, α-naphthylamine, and mono- and diethylanilines. It was found that the reaction gives methyl nitrite and the respective free amines.

2. Diethylaniline nitrite was prepared for the first time.

3. It was established that C- and N-nitroso compounds do not react with diazomethane.

4. The error of identifying the so-called amine nitrites with N-dihydroxyhydrazines was demonstrated.

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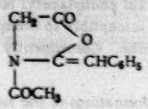
α-SUBSTITUTED α-AMINO ACIDS

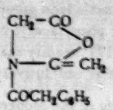
II. STRUCTURE AND PROPERTIES OF THE PRODUCT OF REACTION OF PHENACETURIC ACID WITH ACETIC ANHYDRIDE

S. I. Lure, E. S. Chaman and M. M. Shemyakin

It is known that the majority of acylated α-amino acids are transformed into the corresponding oxazolinones on heating with acetic anhydride. On reaction of phenaceturic acid with acetic anhydride, however, a crystalline compound (m. p. 176-177°) is formed which is not the usual oxazolinone. For this compound, first described by us [1] in 1949 and simultaneously by American investigators [2], three formulas were proposed – (I), (II) and (III) – the last of which was immediately rejected as being untenable, while of the others the most probable is formula (I), although conclusive evidence of its correctness was not obtained.



(I)



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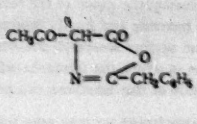
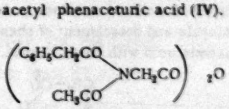


(III)

In 1953 I. T. Strukov [3], without citing the preceding investigations, again described the reaction of phenaceturic acid with acetic anhydride and arrived at the conclusion that one of the products isolated by him (a substance with m. p. 175-177°) was the anhydride of N-acetyl phenaceturic acid (IV).



(IV)

A comparison of the conditions of formation and the properties of the substance with m. p. 176-177° described by us and of the substance with m. p. 175-177° described by I. T. Strukov led us to the idea that they were identical. To test this supposition, we prepared both compounds with observance of all the described conditions of their synthesis, and we compared and again analyzed the products isolated. As had been expected, they proved to be identical with one another; the analytical data and the results of determination of their molecular weight corresponded to the values calculated for the formulas (I) and (II), and they differed considerably from the values calculated for formula (IV). The results obtained indicate that the substance described by us, by the American workers and by I. T. Strukov cannot be the anhydride of N-acetylphenaceturic acid (IV), and that the structure of the compound corresponds to formula (I) or (II).

A final solution in favor of one of these formulas could, in our opinion, be reached most simply by a study of the bromination of the substance. If its structure corresponded to formula (I), then addition of bromine at the heptacyclic double carbon–carbon bond and subsequent careful hydrolysis of the product of bromination ought to lead to formation of α-bromophenylacetic and aceturic acids; but the presence in the hydrolysis products of bromoacetic and phenaceturic acids would point to the structure represented by formula (II).

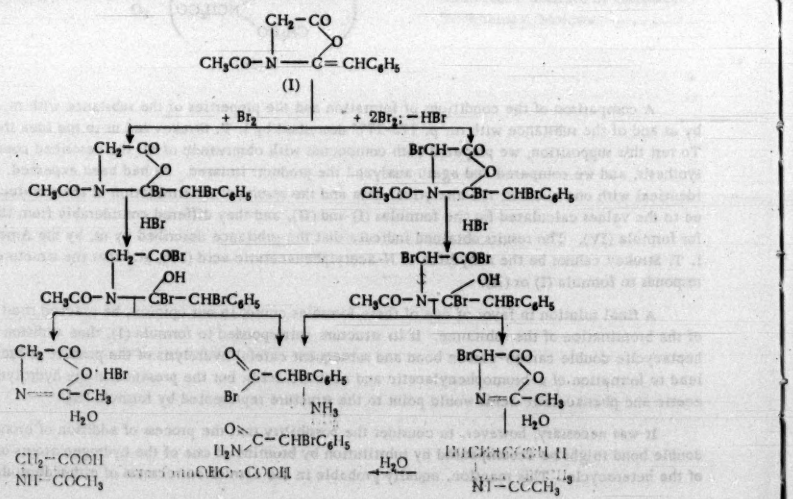
It was necessary, however, to consider the possibility that the process of addition of bromine atoms at the double bond might be accompanied by substitution by bromine of one of the hydrogen atoms of the methylene group of the heterocycle. This reaction, equally probable in the case of correctness of either formula (I) or (II), was

recently observed by us with various oxazolinones [4]. It proceeds with particular facility with oxazolinones that are not substituted in the 4-position and is realized in this case with consumption of only 0.5 mole bromine, since the hydrogen bromide evolved during the bromination reacts in the instant of formation with still unchanged starting oxazolinone, transforming it into the hydrobromide of the oxazolinone or into the acid bromide of the corresponding α-acylamino acid.

Bromination of the substance with m. p. 176-177° investigated by us, carried out in a medium of dry dichloroethane at a low temperature, showed that this reaction actually consumes not 1 but 1.5 moles bromine, since the latter not only adds on at the heptacyclic double bond but also substitutes one of the hydrogen atoms of the methylene group of the heterocycle (see scheme). During bromination a hydroscopic precipitate separates out which is the hydrobromide of the oxazolinone of aceturic acid (or its acid bromide); it is readily converted by the action of water into aceturic acid, and aniline converts it into the anilide of the latter. From the reaction solution, following treatment with ammonia, was isolated the amide of α-bromophenylacetic acid in a yield of up to 60%, thus indicating that the solution contained α-bromophenylacetyl bromide. Moreover, treatment of the reaction solution with aqueous sodium carbonate solution gave glyoxylic acid; this was formed from the corresponding bromooxazolinone via α-hydroxy-α-acetylaminoacetic acid which under these conditions readily undergoes hydrolytic cleavage.*

The isolation of the above-noted final compounds permits us to conclude that the substance with m. p. 176--177° possesses the structure expressed by formula (I). The process of bromination of this substance and the later transformations of the products of bromination are represented in the scheme, so that their more detailed consideration would be superfluous. We rejected another sequence of reactions (bromination in the original compound of only the methylene group of the heterocycle, subsequent cleavage of the molecule under the influence of the evolved hydrogen bromide and finally bromination of the methylene group of the resultant phenylacetyl residue) for the reason that neither N-acetyl-phenylacetamide nor phenylacetyl bromide were susceptible to bromination under the conditions in which the substance with m. p. 176-177° readily reacts with bromine. Consequently the question of the structure of this substance can now be regarded as conclusively settled.

In conclusion we may note that during a study of the properties and transformations of the substance with m. p. 176-177°, we attempted to prepare its 4-benzylidene derivative. The condensation of this compound with benzaldehyde could only be effected, however, under fairly drastic conditions (prolonged heating in a medium of acetic anhydride in presence of potassium carbonate at 100-110°); for this reason, in place of the anticipated condensation product we obtained 2-methyl-4-benzylidene-oxazolinone-5 and α-phenylcinnamic acid. These compounds were evidently the result of a whole series of reactions: condensation of the starting compound with benzaldehyde, opening of the heterocycle and detachment of phenylacetic acid, reformation of the heterocycle, and, finally, condensation of phenylacetic acid with benzaldehyde.



* For fuller details of this type of transformation see [4].

EXPERIMENTAL

Bromination of 2-benzylidene-3-acetyl-oxazolidinone-5 (I) 5 g thoroughly pulverized oxazolidinone (I) were stirred with 20 ml dry dichloroethane, and to the viscous mass at 7-9° was added, dropwise, a solution of bromine in dichloroethane until a permanent orange color had been imparted to the mass. In all 5.4 g bromine was consumed. The crystalline precipitate of 2-methyl-oxazolinone-5 hydrobromide was filtered and triturated with water; yield 0.65 g (24%) aceturic acid with m. p. 200-203°. Introduction of the precipitate of hydrobromide into a benzene solution of aniline led to formation of aceturic acid anilide; prisms with m. p. 191-193°.

Into the dichloroethane filtrate, with cooling and stirring, was run 20-25 ml 25% aqueous solution of ammonia. Crystals came down and were filtered and washed with water. Weight 2.9 g (59%); m. p. 138-141°. After recrystallization from aqueous alcohol the compound melted at 143-145° and did not give a depression in admixture with α-bromophenylacetamide.

Reaction of 2-benzylidene-3-acetyl-oxazolidinone-5 with benzaldehyde. 4 g oxazolidinone (I), 2.5 g freshly distilled benzaldehyde, 2.5 g calcined potassium carbonate and 12 ml acetic anhydride were heated 2 hours at 100-110°. The cooled reaction mixture was stirred with water and ice; the resultant oil was twice washed with iced water by decantation. The brown oil was triturated with alcohol, the crystals were filtered, triturated with toluene and again filtered. Weight 0.25 g. After two recrystallizations from methyl alcohol the compound melted at 149--152° and did not give a depression in admixture with 2-methyl-4-benzylidene-5-oxazolinone synthesized from benzaldehyde and aceturic acid [5].

The aqueous acetic acid and alcoholic mother liquors (see above) were combined and heavily diluted with water. The precipitated crystals were twice recrystallized from toluene. The compound melted at 170-172° and did not give a depression in admixture with α-phenylcinnamic acid.

SUMMARY

It was proved that the substance obtained on reaction of phenaceturic acid with acetic anhydride is 2-benzylidene-3-acetyl-oxazolidinone-5.

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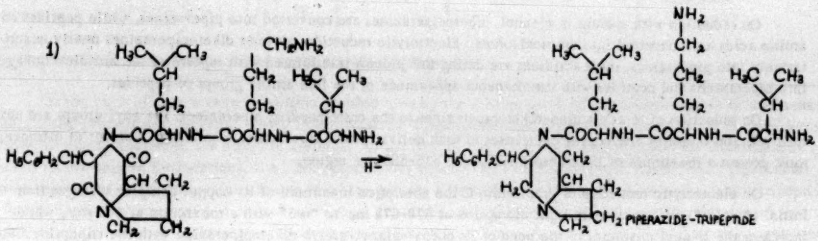
* T. p. = C. B. Translation Bureau.

CONCERNING THE NUMBER OF CYCLIC α-AMINO BONDS OF AMINO ACIDS IN SOME PROTEINS

N. I. Gavrilov and P. G. Ioanisiani

One of us in collaboration with A. V. Koperina [1-4] developed a method of quantitative determination of cyclic anhydrides of amino acids in the protein molecule. It was based upon the facility with which these anhydrides are converted on electrolytic reduction into saturated heterocyclic amines – piperazines. The linear anhydrides (polypeptides) are not reduced under these conditions. Protein may contain two forms of bond between diketopiperazines and tripeptides, as for example in the structure of gramicidin C: 1) The N-acylamino bond and 2) the N-amidino bond

1)



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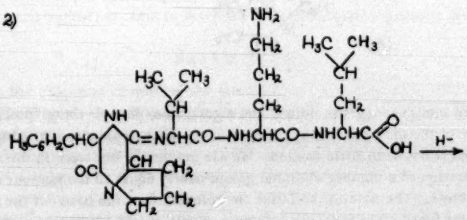
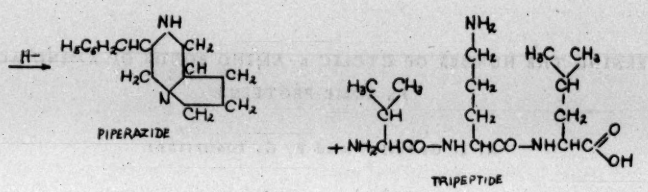




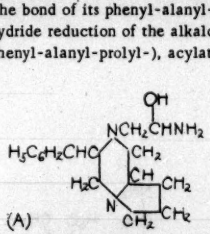
On electrolytic reduction the N-acylamino-tripeptide bond is reduced to tripeptide-piperazide, while the piperazine-tripeptide amidine bond is reduced with scission of the amidine group to tripeptide and piperazine.

Many authors have used the method of reduction of diketopiperazines to piperazines [5-11]. Thus, the reduction of N-acylamine-diketopiperazine by Stoll's method with lithium aluminium hydride leads to formation of N-substituted piperazines [11].

On reduction with sodium in alcohol, diketopiperazines are converted into piperazines, while peptides and amino acids are converted into aminoalcohols. Electrolytic reduction converts diketopiperazines nearly quantitatively into piperazines; their amidines are during this process transformed with rupture of the amidine linkage into piperazines and peptides with simultaneous appearance of the free amino groups of peptides.

On reduction of N-acylamino-diketopiperazines to the corresponding piperazines, the acyl groups are not split off, and therefore the copper complexes of such derivatives of piperazines, containing 4 atoms of nitrogen, must possess a maximum of light absorption in the 515-525 mμ region.

On electrolytic reduction of gramicidin C the absorption maximum of its copper complex changes from the initial ("violet") with maximum light absorption at 570-575 mμ to "red" with a maximum at 535 mμ, which indicates the N-acyl character of the bond of its phenyl-alanyl-prolyl-diketopiperazine with the tripeptide. Stoll [10] effected lithium aluminium hydride reduction of the alkaloid ergotamine and obtained piperazine originating from the same diketopiperazine (phenyl-alanyl-prolyl-), acylated at the nitrogen of α-amino-β-hydroxypropionic acid (A).



(A)

Consequently in both substances (gramicidin C and ergotamine) phenyl-alanyl-prolyl-diketopiperazine was linked with the remainder of the molecule at the nitrogen of the phenyl-alanine. It is highly probable that this bond occurs in proteins, but it has been little studied. We are continuing our work in this direction. Reduction of amidines results in liberation of a number of amino groups nearly equal to the number of amidine bonds (see scheme), as seen from Table 1. The data in the latter are calculated on the basis of the ratio between the tripeptides and the piperazines found by us [13] (see column 1, Table 1). In column 3 is given the amount of nitrogen of the tripeptides participating in the formation of the amidine bond on the basis of determination of the copper numbers [14]. Column 4 illustrates the increase in amount of amino nitrogen (in percentages of that experimentally found by the Slyke determination in the course of 5 minutes) which had been freed during electrolytic reduction. Comparison of columns 3 and 4 does not reveal a great difference between the calculated and the experimental values (with exception of gelatin which was studied by Ionanisiani •). Only in the case of gliadin is the amount of amino nitrogen liberated during reduction slightly larger than the calculated amount, probably due to partial hydrolysis.

• Data of the present investigation.

TABLE 1

Amount of amino nitrogen after electrolytic reduction

Protein	Ratio of tripeptides to diketo-piperazines	Nitrogen (in percent of total)		Increase in amount of amino nitrogen after reduction	Author
		In piperazines			
		Total	Amidino		
	1	2	3	4	
Gelatin	2:2	23.6	11.8	17.9	Ioanisiani*
Gelatin	3:2	27.6	20.8	20.8	Koperina [3]
Gliadin	1:1	26.5	13.25	17.6	Ioanisiani
Casein	4:3	22.9	15.3	14.0	"
Plastein	2:1	16.2	16.2	14.4	"
Edestin	3:2	18.1	13.8	13.9	"
Blood albumen	8:5	21.6	17.3	18.0	Koperina [3]
Sturin sulfate	2:1	8.4	8.4	6.4	"
Gramicidin C	1:1	32.2	16.1	13.9 (19.8)	Ioanisiani
(Dimer)	2:2				

* The data of P. G. Ioanisiani relate to the present investigation.

On the basis of such a ratio it became possible to carry out a calculation of the structural units in the monomers of the investigated proteins. Thus, in sturin sulfate 1 piperazine corresponds to 2 tripeptides, i. e., both keto groups in diketopiperazine are bound to amidine. In the case of blood albumen 5 diketopiperazines correspond not to 10 but only to 8 tripeptides, i. e., both piperazines contain two free keto groups. Casein has 3 piperazines for 4 tripeptides, which also results in two free keto groups. Gliadin has a more complex structure, and 1 tripeptide corresponds to 1 piperazine, i. e., we should expect gliadin to contain at least one N-acylamino linkage (as in gramicidin C) and one free keto group in each piperazine. Edestin has only one free keto group for two piperazines, just as in the case of gelatin. The dimer of gramicidin C contains two keto groups and two N-acylamino linkages.

These facts are reflected in the results of reduction. Thus, in the case of reduction of a compound with only an amidino linkage, one or two amino groups (in the case of mono- or diamidine) are liberated for each titratable nitrogen. But on reduction of a compound containing both an amidine and an aminoacyl bond, appearance of amino nitrogen is again observed but possibly without formation of piperazine susceptible to titration. If we assume the presence of only amidino bonds and if we calculate (from the ratio between the tripeptides and the diketopiperazines present in the protein molecule) the number of amino groups that ought to be formed on electrolytic reduction, it is found that this number is close to that experimentally found and given in Table 1.

EXPERIMENTAL

Procedure. With the objective of making the procedure more widely applicable we went over to the microdetermination of amino nitrogen. One of us [15] had improved the method of Slyke [16] and Tsuverkalov [17] for determination of amino groups; for determination of nitrogen by the formaldehyde method (Sörensen) we employed potentiometric (not indicator) titration with the glass electrode [18]. Electrolytic reduction was performed essentially by the method developed by A. V. Koperina [3]; the apparatus, however, was slightly modified, a gramophone turn-table being used for agitation of the mercury cathode. Into an ice-cooled crystallizer was put the electrolytic reduction cell containing mercury on its base to serve as cathode. The thermometer and the platinum electrode were made to stir the mercury by movement of the gramophone turn-table. The mercury used for electrolytic reduction was purified by vacuum distillation (once) followed by simple washing with nitric acid and numerous washings with distilled water. The solution for electrolytic reduction (transparent and free from turbidity) was introduced over the mercury and into it was lowered a porous vessel with a condenser, an anode and an anode liquid. Reduction was performed both in aqueous and in acetic acid solutions containing 5% of hydrochloric acid in the given solution. Current density 0.056 A/cm^2. Voltage 13.5 V. Temperature 15-25°. An experiment required 0.1 g protein (0.05% in the cathode solution). The average duration of reduction was 7 hours.

Working up of reduced solutions. The acetic acid, water and hydrochloric acid were distilled off in vacuum at a temperature not higher than 30°, and the distillation was repeated with a fresh portion of water. The solution

developed a positive biuret reaction (violet color) and a negative reaction with picric acid for diketopiperazine. After reduction, the solution was evaporated to dryness and the residue was hydrolyzed with 25% hydrochloric acid. After hydrolysis for 26-30 hours the solution was concentrated in vacuum at 30° and transferred to a 25 ml measuring cylinder. The amino nitrogen in the reduced hydrolyzates was determined by Sörensen's method using potentiometric titration [18]. Titration was carried out at first from pH 7 to pH 9, but subsequently it was found that it would be more correct to select pH 6 at the start. Nevertheless, both at initial pH 7 and pH 6 the difference in the number of determined cyclic bonds proved negligible. In the case of casein the amount of amino nitrogen found after hydrolysis before reduction (at pH 6) was 85.8%; after reduction and hydrolysis it was 74.4%. The fall in amino nitrogen was 11.4% (rings 22.8%). At pH 7 the corresponding values were 82.4 and 71.2%, which gives a fall in amino nitrogen of 11.2% and corresponds to a ring content of 22.4%. Nevertheless we recommend initial titration at pH 6.0, while for proteins the selected pH will depend upon the isoelectric point.

In order to check the correctness of the proposed pH range for formaldehyde titrations (6.0-9.0), and also to explain the titratability of piperazine * in buffer mixtures (of whatever type, for example hydrolyzates of reduced proteins), we prepared an artificial amino acid-piperazine mixture (Table 2) similar in composition to the hydrolyzate of reduced casein. A weighed quantity of amino acid-piperazine mixture (1.0062 g) was dissolved in distilled water in a 250 ml measuring cylinder. The nitrogen content of the solution by the Kjeldahl method was 13.91% (calcd. 13.86%). Gasometric determination of the amino nitrogen gave the following results: 1) 15-minutes' determinations: Found mg nitrogen: 0.356, 0.357; calc. 0.354 (100.7%); 2) 3-minutes' determinations: found mg nitrogen: 0.311, 0.36; calc. 0.328 (95.4%).

Results of the formaldehyde titration of the amino acid-piperazine mixture are set forth in Table 4.

Determinations by the Slyke method only possess an extremely relative value. If such a determination is performed on protein, then the results of 3-minute, and even more of 15-minute, determinations are too high due to the reaction of nitrous acid with lysine, ammonia, and the amides of aspartic and glutamic acids (Table 3). However, the approximate number of NH_2 groups can be determined. Thus, we calculated the number of amino groups liberated on reduction by deducting from the amount of amino nitrogen (after a 3-minute Slyke determination) found after reduction its initial amount as determined by the same method. This amount of final amino groups of the tripeptides can be regarded as linked in monomers with an amidine structure. Table 3 explains the errors in Slyke determinations depending upon the presence of ammonia and lysine.

Determination of rings in gelatin (Table 5). Gelatin was purified by Loeb's method [19]. The total nitrogen (mean of three determinations) was 16.24 %. Moisture content 1.72% at 110°. Amino nitrogen by Sörensen's method (mean of three determinations) was 4.06%; the Slyke determination gave 2.9% (5-minute determination) and 5.05% (30-minute determination).

Hydrolysis of gelatin. 2.9727 g gelatin in 60 ml 25% hydrochloric acid was heated for 24 and 48 hours. After 24-hours' hydrolysis the total nitrogen found was 16.07%; after 48 hours 16.45%. The mean value of amino nitrogen in relation to the total in the hydrolyzate from the first experiment was 79.06%, and in the second experiment it was 81.09%. The amino nitrogen, (theoretically calculated in [20]) must, on the basis of the number of amino groups, be equal by Sörensen's method to 84.5%, and by Slyke's method to 72.10%. Hence the proline nitrogen amounts to 11.95% of the total.

The difference between the amount of amino nitrogen determined by the Sörensen and Slyke methods is 11.8%, which indicates that the whole of the proline is in the rings. On the other hand, if the fall in amino nitrogen content after reduction during the determination (both by the Sörensen and Slyke method) had been the same, then we should have expected to find the proline in the peptide portion.

Calculations for determination of rings and peptides in gelatin (Ioanisiani method) give results somewhat different from those by the Koperina method [3], as is reflected in Table 10. The most probable explanation is that treatment of the gelatin leads to loss of a certain amount of the rings, which also changes the ratio from 2: 3 to 2: 2. In this investigation the rings of gelatin were calculated on the basis of data for electrical reduction by Koperina's method.

Reduction of gliadin (Table 6). Gliadin was obtained by the usual method and thrice reprecipitated from alcohol with ether. No free amino nitrogen was found. Moisture 7.52%, Kjeldahl nitrogen 16.39%. Duration of hydrolysis 29 1/2 hours.

* In piperazine hydrochloride the Kjeldahl nitrogen found was %: 17.56, 17.73; calc. 17.6.

TABLE 2

Composition of amino acid-piperazine mixture

Preparation number	Aminoacids	Percent content of protein	Weight of sample (in g)	Nitrogen content of sample (in mg)	Amount of nitrogen that should be found (in mg)	
					Gasometrically	by formaldehyde titration
1	Piperazine	–	0.2001	35.22	–	17.61
2	Arginine	4.1	0.0501	13.81	3.327	3.327
3	Histidine	2.5	0.0371	6.834	2.278	2.278
4	Tyrosine	6.4	0.0659	5.091	5.091	5.091
5	Tryptophan	1.8	0.017	2.331	1.165	1.165
6	Phenylalanine	5.2	–	–	–	–
7	Methionine	3.5	0.0075	0.874	0.874	0.874
8	Cystine	0.36				
9	Threonine	3.9	0.04	4.701	4.701	4.701
10	Proline	8.2	–	–	–	–
11	Glycine	0.5	0.0607	9.537	9.537	9.537
12	Alanine	5.6				
13	Leucine	12.1	0.1211	12.925	12.925	12.925
14	Glutamic acid	22.8	0.1198	11.401	11.401	11.401
15	Aspartic acid	6.3	0.0637	6.700	6.700	6.700
16	Serine	6.5	0.0664	8.845	8.845	8.845
17	Valine	7.0	0.0704	8.416	8.416	8.416
18	Lysine	6.9	0.0864	13.241	13.241	13.241
	Total	103.6	1.0062	139.426	88.501	106.111

TABLE 3

Determination of nitrogen by the Slyke method in ammonia and lysine (in the Ioanisiani apparatus)

	Content of nitrogen in sample (in g)	Duration of Slyke determination (in minutes)					
		3	5	7	10	15	30
Ammonium chloride:							
in grams	0.558	0.087	–	–	–	0.340	–
in percent	–	15.6	–	–	–	61.1	–
Lysine							
in grams	0.322	0.197	0.230	0.253	0.280	0.311	0.309
in percent	–	61.2	–	–	–	–	90.0

TABLE 4

Formaldehyde determination of amino acid-piperazine mixture

Conditions of performance of formaldehyde titration	Nitrogen taken (in mg)	Nitrogen found (in mg)	Nitrogen found (in %)
Potentiometric titration (pH 6.0-9.0)	0.848	0.856	100.9
	0.848	0.856	100.9
	0.848	0.848	100.0
Potentiometric titration (pH 7.0-9.0)	0.848	0.812	95.8
	0.848	0.819	96.6
	0.848	0.819	96.6
Sörensen-Gavrilov titration*	10.61	10.38	97.8
	10.61	10.52	99.1

* First stage – neutral, red-pink solution, pH 6.5. Third stage – phenolphthalein, deep crimson color, pH 9.0.

TABLE 5

Analysis of forms of nitrogen in gelatin during electrolytic reduction

	Amino nitrogen (in percent of total nitrogen)		
	By Sörensen's method (pH 7.0-9.0)	By Slyke's method	
		5 minutes	30 minutes
Before reduction and before hydrolysis	4.06	2.89	5.05
After hydrolysis	81.9	71.3	84.0
Before reduction and before hydrolysis	39.9	34.8	–
After reduction and after hydrolysis	70.1	58,1	70.0
Fall in amino nitrogen content	11.8	13.2	14.0
Number of rings	23.6*	13.2	–

* Koperina's method gives 27.6%.

TABLE 6

Analysis of forms of nitrogen of gliadin during electrolytic reduction

	Total nitrogen	Amino nitrogen (in per cent of total	
		By Sörensen method (pH 7.0-9.0)	By Slyke method (5 minutes)
Hydrolysis	16.64	78.69	56.9
Electrolyitc reduction	16.42	34.5	17.6
Electrolytic reduction followed by hydrolysis	16.46	65.35	47.6
Fall in amino nitrogen content	–	13.24	9.3
Number of rings	–	26.5	–

TABLE 7

Analysis of forms of nitrogen of casein during electrolytic reduction

	Total nitrogen	Amino nitrogen (in percent of total)			
		By Sörensen's method		By Slyke's method	
		(pH 7-9)	(pH 6-9)	3 minutes	5 minutes
Before hydrolysis	14.85	8.5	8.15	3.7	7.4
Hydrolysis	14.89	82.4	85.85	62.8	81.8
After reduction	14.75	–	37.0	17.8	26.2
After reduction and hydrolysis	14.70	71.4	74.4	51.1	70.8
Fall in amino nitrogen	–	11.4	11.4	11.7	11.0
Number of rings	–	22.8	22.8	–	–
Proline	–	–	11.6	–	–

TABLE 8

Analysis of forms of nitrogen in plastein from casein during electrolytic reduction

	Total nitrogen	Amino nitrogen (in percent of total)		
		By Sörensen's method (pH 6-9)	By Slyke's method	
			3 minutes	5 minutes
Before hydrolysis	13.77	0	2.6	4.6
Hydrolysis	13.68	76.3	61.6	77.0
Ammonia	–	6.3	–	–
After electrolytic reduction	–	27.0	14.4	20.97
After electrolytic reduction and hydrolysis	13.80	68.19	49.4	66.6
Fall in amino nitrogen	–	8.1	12.2	10.4
Amount of nitrogen in rings	–	16.2	–	–

TABLE 9

Analysis of forms of nitrogen of edestin during electrolytic reduction

	Total nitrogen	Amino nitrogen (in per cent of total)		
		By Sörensen method (pH 6.0-9.0)	By Slyke method	
			3 minutes	15 minutes
Hydrolysis	18.6	71.0	59.7	70.5
After electrolytic reduction	18.33	27.5	15.5	20.8
After electrolytic reduction and hydrolysis	18.5	62.0	47.1	56.3
Fall in amino nitrogen	–	9.0	12.6	15.2
Amount of nitrogen in rings	–	18.0	–	–
Proline	–	4.6	–	–

TABLE 10

Amount of cyclic and chain forms of bonds in some proteins

Protein	Total nitrogen (in %)	Nitrogen of amino groups to total nitrogen (in %)	Nitrogen of cyclic forms of bonds (in %)		Nitrogen of peptide forms of bonds (in %)	
			to total nitrogen	to nitrogen of amino groups	to total nitrogen	to nitrogen of amino groups
Gelatin	18.0	85.5	23.5	27.6	62.9	72.4
Gliadin	17.66	65.2	26.5	46.8	48.7	59.2
Casein	15.76	73.8	22.9	31.03	50.9	69.0
Plastein	13.9	70.1	16.2	23.1	47.0	76.9
Edestin	18.55	58.4	18.1	30.9	40.3	69.0

TABLE 11

Relative number of diketopiperazines and tripeptides in various proteins (in round numbers)

Protein	Number	
	of diketopiperazines	of tripeptides
Gelatin	2	2
Gliadin	1	1
Casein	3	4
Plastein	1	2
Edestin	2	3

Gliadin contains 65.2% of α-amino groups, of which 43.8% of the nitrogen is in the rings. The tripeptide portion is 56.2%. This corresponds to a ratio of 1 tripeptide to 1 diketopiperazine (6 : 7). Consequently we may expect gliadin to have a structure like that of gramicidin C [12].

Reduction of casein. Casein was reprecipitated in its isoelectric state and then subjected to electrophoretic analysis by the Tiselius method in a veronal buffer (pH 11.0). A 2.5% solution of casein in veronal buffer was dialyzed against veronal at a temperature of + 3–5° for 3 days. The veronal buffer was changed twice in each 24 hours. Electrophoresis was carried out at +1–2° for 3 hours 50 minutes, at 60 V, 8 ma. The casein was found to be electrophoretically heterogeneous and was separated into two portions. The first part formed 61.3% of the total weight of casein, the second 38.7%. The electrophoretic mobility of the first was $7.34 \cdot 10^{-5}$, of the second $5.87 \cdot 10^{-5}$ $cm^2\ V^{-1}\ sec.^{-1}$.

As a check on the procedure, a blank experiment of all the determinations was run with casein without electrolytic reduction. 101.3 mg casein was put in the reduction apparatus under the same conditions of acidity and temperature. This control solution was evaporated in vacuum under the same conditions as in normal reduction, and transferred to a measuring flask in which nitrogen was determined by the Kjeldahl method. The amount found was 14.8%. The Slyke nitrogen determination (15 minutes) gave in the sample before evaporation 7.4% of the total nitrogen, and after evaporation (due to hydrolysis) 11.7%. Thus, electrolytic reduction followed by evaporation gives an increase of amino nitrogen not exceeding 4% of the total nitrogen. It is necessary to note that during electrolytic reduction the possibilities of hydrolysis are reduced considerably in comparison with the blank. Thus, firstly, the amount of acid is greatly reduced, and toward the end of the experiment the solution becomes weakly acid; secondly, due to the reduced acidity the vacuum distillation of the water also proceeds under a weakly acidic reaction. Solution of the casein during electrolytic reduction required 5% hydrochloric acid. A 0.05%

casein solution with pH 1.5 was prepared by S. S. Perov's method [21]. Such a transparent solution readily conducts current. However, the hydrochloric acid which moves to the anode causes gradual precipitation of the casein, and therefore it is necessary to introduce hydrochloric acid dropwise (d 1.19) to the solution during the whole period of reduction.

As we see from the data of Table 7, the fall in amino nitrogen as determined by the Sörensen and Slyke methods was the same and was equal to the nitrogen content of proline. According to Table 1, the ring/tripeptide ratio in casein is 3:4 and reduction should liberate 15.3% α-amino nitrogen, whereas actually only 14.0% was liberated. We may explain this by assuming that in casein (more correctly in its monomer) the tripeptide is partly linked to diketopiperazine through the acyl at the nitrogen.

Reduction of plastein, prepared from casein, by Danilevsky's method (Table 8). Plastein was prepared by K. S. Makarov from the casein described in the preceding experiment [22]. The total nitrogen content of plastein was 13.9%, moisture 3.61%, amino nitrogen was not found by Sörensen's method. Electrophoretic analysis (Tiselius) gave one peak, which indicated its homogeneity. Mobility $9.73 \cdot 10^{-5}$ cm^2 V^{-1} $sec.^{-1}$.

Table 10 shows that plastein from casein contains considerably fewer cyclic forms of bonds than casein (16.2% instead of 22.9%). Consequently our earlier assumption [23] that plastein formation is accompanied by cyclization is not justified. As was later shown [24], in the fermentation of gelatin by pepsin, about 6% of the diketopiperazines is split off. It is possible that also during the formation of plastein the diketopiperazines, which had been split off under the previous action of pepsin, no longer enter into the structure of plastein which had been formed by polymerization of monomers already partly deprived of rings. This aspect is considered more fully in [22, 25].

Reduction of edestin. Edestin (Kahlbaum preparation) was recrystallized from a warm solution of sodium chloride. Total nitrogen (Kjeldahl) 18.55%. Amino nitrogen (Slyke – 15 minutes) 2.53%. Amino nitrogen was not determined by the Sörensen method. Sörensen titration (potentiometric) was performed at pH 6 to pH 9 (Table 9).

Edestin contains 58.4% α-amino nitrogen. The amount of cyclic nitrogen, calculated on the total α-amino nitrogen, will be 30.9%.

EVALUATION OF RESULTS

Our investigation has led to improved methods both of electrolytic reduction itself and of analysis of the hydrolyzates. This, in turn has permitted us to use a smaller weight of protein during the determination and to simplify the determination itself.

Evaluation of the amount of diketopiperazines and amidines and their derivatives in the protein molecule should be based upon data for reduction and for determination of the amino nitrogen by the Sörensen method and not by the Slyke method. The latter method gives satisfactory results when applied to amino acids, but does not give consistent results with mixtures of amino acids containing ammonia and in part lysine or proteins. The gasometric method is particularly untrustworthy when applied to analysis of polypeptides [26].

According to recent investigations [27, 28] gelatin is not a homogeneous protein but a heterogeneous mixture. The gelatin that we examined contained considerably fewer rings and α-amino groups. This phenomenon is also reflected in the work of S. G. Ponomarev [27].

The data of Table 10 show that the investigated proteins contain about 30% of their bonds in rings, and only plastein from casein lost about one-quarter of its cyclic nitrogen.

Analysis of the products of reduction of proteins shows that the majority of the bonds between the piperazines and the tripeptides have an amidine structure. Their number fluctuates between 15 and 20% of the total α-amino groups. It is evident that only in exceptional cases is the monomer structure such that both keto groups of diketopiperazine are linked to the tripeptides by an amidino bond (Table 11).

Finally, these facts do not exclude the possibility that a certain number of free groups of the tripeptides is acylated at the nitrogen of the piperazines of other monomers, as we find in gramicidin C (see scheme).

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INVESTIGATION OF THE ALKALOIDS OF THE SEEDS OF LOLIUM CUNEATUM (NEVSKI)

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Among the plants of the family of the Gramineae the number of known varieties containing alkaloids is still very small.

One of the most thoroughly studied alkaloid-bearing varieties is the reed, Orundo donax, indigenous to Central Asia, from which in 1935 A. P. Orekhov and S. S. Norkina [1] isolated a new alkaloid to which the name donaxine was given. The same alkaloid was found by Euler [2] in some varieties of barley and named gramine. Wieland [3] realized the synthesis of gramine. From oats was isolated the alkaloid hordenine [4] whose structure was also established.

The species Lolium also belongs to the family of the Gramineae. The seeds of Lolium temulentum [5] contain the alkaloid temuline with the composition $C_7H_{12}N_2O$. The literature does not give its physical or chemical properties.

From Lolium perenne [6] were isolated two alkaloids: perloline with the composition $C_{36}H_{22}N_4O_8(OCH_3)_4 \cdot H_2O$, and perlolidine with the gross formula $C_{25}H_{18}N_4O_2$. The latter can also be obtained by oxidation of perloline. These are the only scanty data on the alkaloids of the Gramineae.

Nine varieties of Lolium grow in the territory of the Soviet Union [7], of which six are indigenous to Central Asia [8]. Notwithstanding the toxicity of these plants (especially the seeds) they have not hitherto been chemically investigated. In connection with a study of the alkaloids of all poisonous weeds, including their seeds and fruits, which choke cultivated fields in Central Asia, we began an investigation of the alkaloids of L. cuneatum (the local name is "mastak" – a darnel). This is extremely common in the cornlands of Central Asia, particularly in Southern Uzbekistan. The use of grain not freed from darnel may cause poisoning.

The toxicity of L. cuneatum (temulentum) was mentioned as far back as 1869 by A. P. Fedchenko [9], the famous traveler and explorer of Central Asia; he also discovered a characteristic reaction for the presence of traces of darnel in flour. To a sample of the flour is added sufficient alcohol to cover the flour. Addition is then made of one or two drops of concentrated sulfuric acid. If the flour contains darnel, even in the form of meal, the whole mass acquires a more or less deep red color depending upon the amount of toxic ingredient. We confirmed the efficacy of this reaction in several experiments. It was established that the mixture of alkaloids isolated from L. cuneatum does not give this qualitative reaction. It must be assumed that the color is not derived from the alkaloids but from other substances present in the seeds of L. cuneatum.

In 1951 the botanical expedition of the Institute of Chemistry of the Academy of Sciences of the Uzbek SSR, under the leadership of E. E. Korotkova, collected ripe seeds of L. cuneatum in three rayons of Kashka-Darinskaya and in oblasts of Surkhan-Darinskaya. The seeds collected in the Kitabsk rayon, where they contaminated the wheat, contain 0.4% of a mixture of alkaloids, while those in the Denausk rayon (found in crops of hemp *) contain 0.3%. Finally, the seeds of L. cuneatum picked in the Kassan rayon from wheat contained 0.25% of a mixture of alkaloids. This shows that the content of alkaloids in the seeds of L. cuneatum depends, apart from other factors, on the place of growth of the plant itself [10].

Since the seeds of darnel (containing 0.25% of a mixture of alkaloids) were prepared in large quantity, we made a thorough chemical study of the alkaloids of this weed.

The alkaloids in the form of the free bases were extracted from pulverized seeds of L. cuneatum with dichloroethane; further working up by the usual methods gave a fairly mobile liquid mixture of alkaloids with a pale-yellow color. This mixture was separated into two parts: one distilling in vacuum (2-5 mm) and a non-distilling alkaloid fraction. The second part is a solid whose investigation is at present proceeding.

* Translator's note. "Hemp" is given with some reserve. The Russian term does not appear in the available dictionaries. There is only indirect evidence that "hemp" is correct.

From the first (liquid) portion, constituting 55% of the mixture, we succeeded (by further fractional distillation in vacuum and purification in the form of salts) in isolating and characterizing three alkaloids in the pure form. Since they all differed in properties from known alkaloids described in the literature, we named them lolinidine, loline and lolinine.

The lolinidine, (b. p. 85-93° at 5 mm), separated from the first liquid fraction of the mixture of bases, was so strong a base that even on standing in the air it slowly deposits crystalline lolinidine carbonate (the process is accelerated if carbon dioxide is passed through). Lolinidine gives a crystalline hydrochloride and methoiodide.

The alkaloid loline is a colorless and odorless liquid, boiling at 103° (5 mm). The empirical formula is $C_8H_{14}N_2O$. Loline gives a series of nicely crystallizing salts, the most characteristic of which are the dihydrochloride, dihydrobromide and dinitrate. The possibility of formation of the monoacid salts also shows that the nitrogen atoms in the molecule of the alkaloid possess differing degrees of basicity. Boiling of loline with acetic anhydride gives crystalline N-acetylloline. With benzoyl chloride in an alkaline medium it gives N-benzoylloline. With nitrous acid the alkaloid gives the nitroso derivative in good yield. Quantitative determination established that loline contains one N-methyl group. Methylation with formaldehyde and formic acid readily gives N-methylloline; the latter forms a dihydrochloride, dihydrobromide, monomethoiodide, dinitrate and dipicrate. All these reactions show that one of the nitrogen atoms of loline is secondary and the other tertiary.

Reaction of loline with methyl iodide gives three substances: loline hydroiodide methoiodide, loline hydroiodide, and a substance identical with N-methylloline monomethiodide. The mechanism of this reaction is the following: The tertiary nitrogen atom of loline normally forms a methoiodide, while the secondary nitrogen atom, as is usual, forms the hydroiodide of the N-methyl-base; at the same time the molecule of loline which has not succeeded in entering into reaction behaves like a strong base in removing hydrogen iodide from the weakly methylated base and so forms loline hydroiodide.

During acetylation and benzoylation the oxygen atom of loline behaves inertly, thus reflecting the presence of a carbonyl group in loline. Since loline is a secondary-tertiary, strong diacidic base, we must assume that the carbonyl group is not adjacent to nitrogen.

Loline is a saturated compound and does not undergo catalytic hydrogenation. Consequently loline has the extended formula: $C_6H_{10}(CO)(NCH_3)(NH)$.

A hydrobromide, crystallizing nicely from methyl alcohol, was obtained from the third fraction. The base, isolated from the hydrobromide, can be recrystallized from anhydrous ether. Analysis showed that lolinine has the formula $C_{10}H_{16}N_2O_2$.

Lolinine gives nicely crystallizing salts; the hydrobromide and perchlorate are characteristic. It contains one methylimido group; both oxygen atoms are inert. In the light of these properties, and comparing the formulas of lolinine $C_{10}H_{16}N_2O_2$ and loline $C_8H_{14}N_2O$, we arrived at the conclusion that lolinine, which differs in composition by one acetyl group, is N-acetylloline. This was confirmed experimentally: loline is formed when lolinine is heated with alcoholic alkali.

Lolinine has the extended formula $C_6H_{10}(CO)(NCH_3)(NCOCH_3)$. Thus, establishment of the structure of loline has also clarified the structure of lolinine.

EXPERIMENTAL

55 g milled ripe seeds of L. cuneatum were moistened with 10% ammonia; and the alkaloids were extracted with dichloroethane in a percolator. The dichloroethane extract was worked up with 15% sulfuric acid to form a thick emulsion which filtered with difficulty. The solution was washed with ether and the mixture of sulfates of bases was decomposed with gaseous ammonia under cooling. The bases were extracted with chloroform. The fluorescing chloroform extract was concentrated to a small volume and dried with calcined sodium sulfate. The residual chloroform was then driven off completely. Yield 142 g or 0.25% of the weight of the seeds.

142 g of the faint-yellow mixture of bases was distilled in vacuum to give the following fractions: 1) b. p. 85-93° (5 mm), 12 g (loline and lolinidine); 2) b.p. 95-110° (5 mm), 25 g (mainly loline); 3) b.p. 145-160° (2 mm), 40 g (mainly lolinine).

Lolinidine

Carbonate. Through the readily mobile liquid, comprising the first fraction, was passed a stream of carbon

dioxide. Crystalline lolinidine carbonate came down and was separated from the other alkaloids by treatment with anhydrous ether. The carbonate was recrystallized from anhydrous alcohol and purified by sublimation; m.p. 102-103°. Yield 5 g. From the mother liquor of the carbonate was obtained 8 g loline hydrochloride.

Lolinidine hydrochloride. Formed by adding an alcoholic solution of hydrochloric acid to the carbonate of the base. It was recrystallized from a mixture of alcohol and acetone. On intense cooling lolinidine hydrochloride separates in the form of colorless, lustrous crystals with m.p. 215-216°.

Methiodide. To an alcoholic solution of the base was added methyl iodide. The reaction mixture was boiled 2 hours until the alkaline reaction had disappeared. After evaporation of the solvent the residue crystallized. After recrystallization from alcohol, the methiodide has m.p. 210-212°.

Loline

Dihydrochloride. 25 g base (fraction 2) was dissolved in 50 ml alcohol; to the solution was added an alcoholic solution of hydrochloric acid until the reaction to congo was weakly acidic. Loline dihydrochloride came down and was separated from the liquid and recrystallized from alcohol. The crystals had m.p. 256-257° (with decomp.). Yield 19 g.

0.9728 g substance in 10 ml water; l 10.0, α_D + 0.60°, $[\alpha]_D^{19}$ + 6.2°.

Found %: Cl 31.25, 32.78. $C_8H_{14}ON_2 \cdot 2HCl$. Calculated %: Cl 32.12.

18 g loline dihydrochloride was dissolved in 100 ml water and to the solution was added 40% sodium hydroxide solution. The free base was extracted with chloroform. After removal of the chloroform the residue was distilled in vacuum. Yield 11 g.

B.p. 103° at 5 mm, b.p. 229° at 731 mm, d^{20} 1.1343, n_D^{22} 1.5505.

0.5560 g substance in 10 ml acetone; l 10.0, α_D + 1.04°, $[\alpha]_D^{20}$ + 18.9°.

Found %: N 18.36, 18.39; NCH_3 6.68, 7.02. M 155.21, 155.00. $C_8H_{14}ON_2$. Calculated %: N 18.16; NCH_3 9.74. M 154.208.

Dihydrobromide. To 2 g loline was added hydrobromic acid dropwise. Loline dihydrobromide crystallized on standing in the form of thick needles which, after recrystallization from alcohol, had m.p. 254-255° (with decomp.). Yield 1.2 g.

0.4292 g substance in 10 ml water; l 10.0, α_D + 0.15°, $[\alpha]_D^{20}$ + 3.5°.

Found %: Br 49.76, 50.72. $C_8H_{14}ON_2 \cdot 2HBr$. Calculated %: Br 50.57.

Loline dihydroiodide. Formed by adding hydriodic acid. On rubbing with a small glass rod a yellowish precipitate came down and after recrystallization from alcohol melted at 233-235° (with decomp.).

1.3200 g substance in 10 ml water; l 10.0, α_D + 0.66°, $[\alpha]_D^{24}$ + 5.0°.

Found %: I 62.71, 61.88. $C_8H_{14}ON_2 \cdot 2HI$. Calculated %: I 61.90.

Mono- and dinitrates. 1 g loline was dissolved in 5 ml acetone and to the solution, with cooling, was added dropwise strong nitric acid until the reaction was neutral. The whole of the solution at once became filled with a thick mass of crystals. After recrystallization from methyl alcohol loline dinitrate had m.p. 148-149°. Yield 0.82 g.

0.6940 g substance in 10 ml water; l 10.0, α_D + 0.43°, $[\alpha]_D^{18}$ + 6.18°.
Found %: C 34.43, 33.96; H 5.92, 5.92; N 19.94, 19.89. $C_8H_{14}ON_2 \cdot 2HNO_3$. Calculated %: C 34.21; H 5.72; N 19.99.

Loline mononitrate was separated from the mother liquor by evaporation. It can also be obtained by adding to the base an insufficient amount of nitric acid. Loline mononitrate was recrystallized from methanol. M.p. 208-210°. Yield 0.25 g.

Found %: C 43.99, 44.19; H 7.08, 7.21; N 19.07, 19.04. $C_8H_{14}ON_2 \cdot HNO_3$. Calculated %: C 44.02; H 6.92; N 19.33.

Perchlorate. To a hydrochloric acid solution of the base was added ammonium perchlorate; colorless, lustrous crystals of loline perchlorate at once came down. M.p. 282° (with violent decomposition).

Sulfate. A few drops of 20% sulfuric acid was added to a solution of loline in methanol; an oil separated

and crystallized after rubbing with a small glass rod. The alcohol was decanted off and the loline sulfate recrystallized from dilute methanol. Long yellow needles with m.p. 250-251° (decomp.).

Dipicrate. To an alcoholic solution of loline was added an alcoholic solution of picric acid. The picrate was recrystallized from water; m.p. 258-260° (decomp.).

Found %: C 38.71, 38.98; H 3.40, 3.61; N 18.23, 18.14. $C_8H_{14}ON_2 \cdot 2C_6H_2(NO_2)_3(OH)$. Calculated %: C 39.09; H 3.60; N 18.23.

Methoiodide. 1.5 g loline was dissolved in 5 ml methanol; to the solution was added 3 ml methyl iodide. The reaction mass was heated until the alkaline reaction had disappeared (2 1/2 hours). Crystals came down on standing. After recrystallization from dilute alcohol loline hydroiodide methoiodide came down as yellowish leaflets with m.p. 210-212°. Yield 0.8 g.

Found %: I 58.74, 58.86. $C_8H_{14}ON_2 \cdot HI \cdot CH_3I$. Calculated %: I 59.85.

The methoiodide of N-methylloline could be separated from the mother liquor by slow volatilization of the solvent. After recrystallization from alcohol, it had m.p. 257-259° (with decomp.). Yield 0.9 g.

0.5160 g substance in 10 ml water; l 10.0 $\alpha_D - 0.25°$, $[\alpha]_D^{30} - 4.84°$.

Found %: I 40.97, 40.81. $C_9H_{16}ON_2 \cdot CH_3I$. Calculated %: I 40.91.

Treatment of the non-crystallizing mother liquor with ammonia gave 0.6 g of unreacted base.

N-Methylloline. To an aqueous solution of 2 g base was added 0.95 g 40% aqueous formaldehyde solution and 0.59 g formic acid (equimolar amounts). The reaction mass was heated in a flask under a reflux condenser on a boiling water bath for 8 hours. The mixture was then cooled and treated with 40% sodium hydroxide solution and subjected to extraction with chloroform. The chloroform extract was dried with calcined potassium carbonate. After driving off the solvent, the product of methylation was distilled in vacuum. Yield 2.1 g.

B.p. 90-91° at 2 mm; d^{20} 1.0172, n_D^{22} 1.4968; 0.9562 g substance in 10 ml methanol; l 10.0, $\alpha_D + 0.89°$, $[\alpha]_D^{31} + 9.31°$.

Found %: NCH_3 13.45, 13.22. M 169.71, 169.90. $C_9H_{16}ON_2$. Calculated %: NCH_3 17.87. M 168.23.

N-Methylloline nitrate. The liquid base was neutralized with nitric acid until weakly acidic to congo. After 24 hours, long needles of N-methylloline nitrate had separated. After recrystallization from methyl alcohol they had m.p. 144-145° (with frothing).

0.4374 g substance in 10 ml water; l 10.0, $\alpha_D + 0.32°$, $[\alpha]_D^{34} + 9.5°$.

Found %: N 19.25, 19.16. $C_9H_{16}ON_2 \cdot 2HNO_3$. Calculated %: N 19.04.

N-Methylloline hydrochloride. 0.5 g base was acidified with 20% hydrochloric acid. Slow evaporation in the air gave crystals which, after recrystallization from a mixture of ether and alcohol, had m.p. 245-246° (with decomp.). Yield 0.4 g.

N-Methylloline dibromohydrate is obtained in exactly the same way. M.p. 198-199 after recrystallization from methyl alcohol.

0.6110 g substance in 10 ml 85% methanol; l 10.0, $\alpha_D + 0.31°$, $[\alpha]_D^{31} + 5.1°$.

Found %: Br 48.00, 48.25. $C_9H_{16}ON_2 \cdot 2HBr$. Calculated %: Br 48.42.

N-Methylloline dipicrate came down on mixing alcoholic solutions of N-methylloline and picric acid. Recrystallized from alcohol; m.p. 183-184°.

Found %: N 18.13, 18.02. $C_9H_{16}ON_2 \cdot 2C_6H_2(NO_2)_3(OH)$. Calculated %: N 17.89.

N-Methylloline methoiodide. 0.5 g base was dissolved in 3 ml methanol and mixed with 1 ml methyl iodide. The mixture was boiled 15 minutes. The residue crystallized after driving off the excess methyl iodide and solvent. After recrystallization from alcohol, N-methylloline methoiodide melted at 258-260°. A mixed test with the compound obtained by methylation of loline (m.p. 257-259°) did not show a depression of melting point. Yield, 0.8 g.

Nitrososloline. 1.3 g loline was dissolved in 20 ml 20% H_2SO_4 and to the acidic solution was added, with cooling and constant stirring, 2.5 g sodium nitrite in 10 ml water. The reaction mixture was stood 24 hours. The next day it was neutralized with sodium hydroxide solution and the reaction products extracted with chloroform. The

chloroform solution was dried with ignited potassium carbonate and the chloroform distilled off. The residue was distilled in vacuum. An oil commenced to come over at 140-145° (2 mm) and crystallized in the receiver. After recrystallization from ether, nitrosololine melted at 64°. Yield 1.2 g.

0.5500 g substance in 10 ml methanol; $\underline{l}$ 10.0, α_D + 1.25°, $[\alpha]_D^{20}$ + 22.8°.

Nitrosololine perchlorate was obtained by adding a solution of sodium perchlorate to a hydrochloric acid solution of nitrosoioline. The liquid became filled with crystals which, on recrystallization from methanol, formed needles with m. p. 195°.

Nitrosololine picrate was prepared by mixing alcoholic solutions of the nitroso base and picric acid. M.p. 194-195° from alcohol.

Reduction of nitrosololine. 1 g nitrosololine was dissolved in 18 ml concentrated hydrochloric acid and heated on a boiling water bath for 2 hours. The solution was then neutralized with sodium hydroxide and the free base extracted with chloroform. Removal of the solvent left 0.85 g brownish product whose identity with loline was proven by the preparation of the hydrochloride, hydrobromide and nitrate. A mixed specimen of the salts with the corresponding salts of loline did not show any depression of melting point.

Acetylloline. 1.5 g base was dissolved in 15 ml acetic anhydride. The solution was boiled 2 hours on a sand bath, after which the acetic anhydride was driven off on a water bath in vacuum. The residue was dissolved in 10 ml water, made alkaline with 25% ammonia, and subjected to exhaustive extraction with chloroform. After removal of the solvent, the product of acetylation was distilled in vacuum. N-Acetylloline came over at 154-156° (2 mm). After recrystallization from anhydrous ether, it melted at 73°. Yield 1.5 g.

Benzoylation. To a mixture of 2 g base and 10 ml 10% sodium hydroxide was added dropwise 1.8 g benzoyl chloride. From the reaction mixture with vigorous shaking was isolated a clotted white product. After 24 hours, the N-benzoylloline was separated and washed with water. Yield 1.6 g. The mother liquor was extracted with chloroform. Removal of the solvent left a further 1.5 g N-benzoylloline. Total yield 3.1 g. After recrystallization from anhydrous alcohol, it melted at 157°.

Found %: N 10.70, 10.62. $C_8H_{14}ON_2 \cdot COC_6H_5$. Calculated %: N 10.84.

Benzoylloline perchlorate. To a hydrochloric acid solution of the base was added a saturated solution of sodium perchlorate. The crystalline perchlorate came down at once. M.p. 194° from methyl alcohol.

Benzoylloline picrate came out in the form of an oil on mixing alcoholic solutions of the base and picric acid. The mother liquor was poured off and a fresh portion of alcohol added to the residue. The solution was heated; thereupon the oil solidified and gradually crystallized. On recrystallization lustrous crystals with m.p. 172° were obtained.

Saponification of N-benzoylloline. 2.5 g N-benzoylloline was dissolved in 40 ml methyl alcohol and to the solution was added 12 g KOH. The solution was heated on a boiling water bath for 4 hours. The alcohol was then evaporated to dryness. The residue was dissolved in a little water and treated with chloroform. After driving off the solvent a liquid residue of loline was obtained, as was proven by preparation of salts and derivatives. Yield 1.5 g.

Lolinine

Lolinine hydrobromide. To 2 g base (fraction 3) with cooling was added dropwise dilute hydrobromic acid. On slow evaporation in the air, lolinine hydrobromide crystallized in the form of cubes which, after recrystallization from methanol, had m.p. 226-227°. Yield 2.3 g.

2 g substance in 10 ml water; $\underline{l}$ 10.0, α_D + 1.50°, $[\alpha]_D^{20}$ + 7.5°.

Found %: Br 28.21, 28.13. $C_{10}H_{16}O_2N_2 \cdot HBr$. Calculated %: Br 28.79.

Lolinine hydrobromide was made alkaline with ammonia and extracted with chloroform. The solvent was distilled off until the solution had a small volume, and the residue was poured into a dish for evaporation. When the chloroform had gone off completely, the residue was rubbed with a glass rod and crystallized. Lolinine had m.p. 73° from anhydrous ether. A mixed test with loline and N-acetylloline did not show a depression of melting point.

0.8806 g substance in 10 ml acetone; $\underline{l}$ 10.0, α_D + 4.50°, $[\alpha]_D^{20}$ + 51.1°.

Found %: N 14.47, 14.25. M 196.04, 197.07. $C_{10}H_{16}O_2N_2$. Calculated %: N 14.27. M 196.244.

Lolinine hydrochloride. To a saturated alcoholic solution of the base was added an alcoholic solution of hydrochloric acid. White crystals started to come down on scratching with a glass rod; their amount increased on cooling. After recrystallization from anhydrous alcohol, lolinine hydrochloride melts at 197-198°.

0.4067 g substance in 10 ml water; l 10.0, α_D + 1.50°, $[\alpha]_D^{20}$ + 36.9°.

Found %: Cl 15.22, 15.34. $C_{10}H_{16}O_2N_2 \cdot HCl$. Calculated %: Cl 15.24.

Lolinine perchlorate was obtained by adding an alcoholic solution of sodium perchlorate to a hydrochloric acid solution of the base. Crystals came down in the form of leaflets after recrystallization from alcohol, had m.p. 174-175°.

Lolinine picrate. The base was dissolved in alcohol and stirred with an alcoholic solution of picric acid, the picrate came down, and after recrystallization from alcohol was obtained in the form of fine crystals with m.p. 195-196°.

Found %: C 45.21, 45.19; H 4.12, 3.96; N 16.61, 16.48. $C_{10}H_{16}O_2N_2 \cdot C_6H_2(NO_2)_3(OH)$. Calculated %: C 45.16; H 4.50; N 16.45.

Methoiodide. 0.5 g lolinine was dissolved in 2 ml methanol; to the solution was added 0.5 ml methyl iodide. The reaction started immediately and went without heating. After evaporation of the solvent, lolinine methoiodide was at once obtained in the form of crystals which, after recrystallization from alcohol, had m.p. 145-146°. Yield 0.9 g.

Found %: I 37.71, 37.81. $C_{10}H_{16}O_2N_2 \cdot CH_3I$. Calculated %: I 37.51.

Saponification of lolinine. 2 g lolinine was dissolved in 50 ml of 20% KOH solution in methanol. The mixture was boiled 2 hours. The alcohol was evaporated to dryness and the residue was stirred with a small amount of water and subjected to extraction with chloroform. After driving off the solvent, the reaction product was distilled in vacuum. An oil started to come over at 102-103° (5 mm); in its properties it was completely identical with loline.

SUMMARY

1. From the seeds of Lolium cuneatum was isolated a mixture of alkaloids; the alkaloid content of the seeds, depending upon the place of growth, was 0.25, 0.3 and 0.4%.

From the portion (55%) of the mixture of alkaloids which distills in vacuum, three new alkaloids were isolated, and were named lolinidine, loline and lolinine.

2. Lolinidine is a liquid and a strong base; it gives a carbonate, hydrochloride and methoiodide. Loline is a diacidic, secondary-tertiary base; it contains a methylimido and a carbonyl group. Lolinine is N-acetylloline.

3. Loline and lolinine have the following formulas:

loline – $C_8H_{14}ON_2$ or $C_6H_{10}(CO)(NCH_3)(NH)$,

lolinine – $C_{10}H_{16}O_2N_2$ or $C_6H_{10}(CO)(NCH_3)(NCOCH_3)$.

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SYNTHESIS OF 3-(β-METHOXYETHYL)-4-METHYLPYRIDINE

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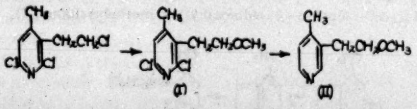
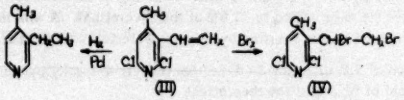
3-(β-Methoxyethyl)-4-methylpyridine is of considerable interest as a starting substance for preparation of various derivatives of pyridine and quinuclidine.

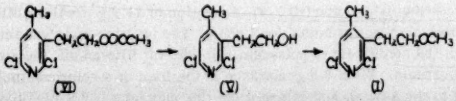
It appeared to us possible to effect the synthesis of this compound by treating 2,6-dichloro-3-(β-chloroethyl)-4-methylpyridine (trichlorocollidine) with sodium methoxide followed by dehalogenation of the 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine according to the scheme:



However, the chlorine atom in the β-chloroethyl group of trichlorocollidine splits off in the form of hydrogen chloride more easily than it enters into the substitution reaction. Thus, for instance, trichlorocollidine does not change when boiled with sodium iodide in acetone or with silver acetate in pyridine, while on reaction with sodium methoxide it forms a mixture of substances which contains about 10% 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine and consists mainly of an unsaturated compound. Reaction of alcoholic potassium hydroxide or silver oxide with trichlorocollidine leads exclusively to an unsaturated compound which is found to be 2,6-dichloro-3-vinyl-4-methylpyridine (III). The structure of (III) was confirmed by its transformation into β-collidine on hydrogenation in presence of palladium black. On reaction with bromine, (III) readily forms 2,6-dichloro-3-(α,β-dibromoethyl)-4-methylpyridine (IV):



For preparation of 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine, the method represented in the following scheme was found more convenient:



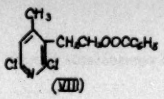
The starting substance was 2,6-dichloro-3-(β-acetoxyethyl)-4-methylpyridine, which is obtained from trichlorocollidine [1]. Alcoholysis of this compound with the help of an alcoholic solution of hydrogen chloride gave 2,6-dichloro-3-(β-ethoxyethyl)-4-methylpyridine (V), the alcoholate of which was transformed by the action of methyl iodide into 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine (I). The alcoholate of 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine was obtained by two methods: 1) direct reaction of (V) with metallic sodium; 2) by the Chugaev reaction.

A study of the first method established that 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine slowly reacts with metallic sodium in a medium of boiling ether, but the reaction does not go quantitatively and is accompanied by formation of a secondary product – 6-chloro-4-methyl-2 3-(2',3'-dihydrofurano)-pyridine (VII). Reaction with metallic sodium also appears to be accompanied by the Wurtz-Fittig reaction with formation of a mixture of dipyridyl derivatives.

Consequently the reaction of 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine with metallic sodium gives

a mixture of the starting substance (V), 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine (I), the dihydrofurano derivative (VII) and a high-boiling fraction consisting apparently of dipyridyls. The high-boiling fraction was separated by vacuum fractionation and was not examined.

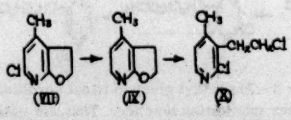
Separation of the mixture of (V), (I) and (VII) was not difficult since (V) and (I), unlike (VII), do not form hydrochlorides, while (V) is readily benzoylated with formation of the high-boiling 2,6-dichloro-3-(β-benzoylhydroxyethyl)-4-methylpyridine (VIII).



(VIII)

The yield of 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine by this method is 40.7% of the theoretical.

It should be noted that the secondary product (VII) is easily dehalogenated by hydrogen in presence of palladium black to form 4-methyl-2,3-(2',3'-dihydrofurano)-pyridine (IX), which by treatment with phosphorus oxychloride at 180° is transformed into 2-chloro-3-(β-chloroethyl)-4-methylpyridine (X).



(VII) (IX) (X)

The second method of preparation of the alcoholate of 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine is based upon Chugaev's [2] observation of the ability of primary alcohols to displace tertiary alcohols with a lower molecular weight from their alcoholates.

On reaction of tertiary potassium isoamyloxide with 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine in boiling toluene followed by treatment of the reaction mass with methyl iodide; 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine was obtained in a yield of 96.7% of the theoretical. Lowering of the reaction temperature to 16-17° led to formation of a mixture of 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine (28%) and 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine (45.9%). Further lowering of the reaction temperature to 0° permitted the yield of methoxy derivative (I) to be raised to 71.6% of the theoretical. It was shown that amylene hydrate (tert-amyl alcohol) can be replaced in this reaction by isopropyl alcohol and metallic potassium by sodium.

Catalytic dehalogenation of 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine gave 3-(β-methoxyethyl)-β-methylpyridine (II) in a yield of 91.3% of the theoretical.

EXPERIMENTAL

2,6-Dichloro-3-vinyl-4-methylpyridine (III). a) A solution of 11.2 g trichlorocollidine and 2.0 g potassium hydroxide in 200 ml anhydrous alcohol was boiled for 8 hours. The reaction mass was acidified with 10 ml concentrated hydrochloric acid, the precipitate of potassium chloride was filtered off, the alcohol was distilled off, and the residue distilled in vacuum. Yield 8.8 g substance in the form of a colorless, mobile liquid with b.p. 142-143° at 16 mm. According to the analysis and composition, this substance is 2,6-dichloro-3-vinyl-4-methylpyridine. Yield 98% of the theoretical. The compound dissolves readily in organic solvents, is insoluble in water, gives a positive reaction for a double bond with potassium permanganate and bromine, and does not form a hydrochloride, picrate or methoiodide; on hydrogenation in presence of palladium black it forms β-collidine.

Found %: C 50.90, 51.05; H 3.98, 3.85; N 7.60, 7.55. $C_8H_7NCl_2$. Calculated %: C 51.06; H 3.73; N 7.45.

b) A mixture of 5.6 g trichlorocollidine, 4.2 g freshly prepared silver oxide and 50 ml dry pyridine was boiled for 6 hours; after cooling, the precipitate was filtered off, the filtrate evaporated in vacuum, and the residue fractionated at 10 mm. Two fractions were collected: 1) with b.p. 136-140°, 2.7 g; 2) b.p. 182-185°, 2.3 g.

The first fraction was a colorless oil giving a positive reaction for a double bond with bromine and with potassium permanganate; it was identified as 2,6-dichloro-3-vinyl-4-methylpyridine. The second fraction crystallized on cooling to form colorless crystals with m.p. 69-70°. The substance was trichlorocollidine. (No depression in mixed melting test with a specimen of trichlorocollidine.)

2,6-Dichloro-3-(α,β-dibromoethyl)-4-methylpyridine (IV). To a solution of 1.88 g 2,6-dichloro-3-vinyl-4-methylpyridine in 15 ml dry chloroform was added a solution of 2.4 g bromine in 10 ml dry chloroform with stirring in the course of an hour. After removal of the chloroform, the residue was distilled in vacuum to give 3.32 g 2,6-dichloro-3-(α,β-dibromoethyl)-4-methylpyridine in the form of a colorless oil with b.p. 177-178° (15 mm). The substance is readily soluble in organic solvents, insoluble in water; it does not form a hydrochloride, picrate or methoiodide.

Found %: C 27.48; H 2.48; N 3.96, 3.93. $C_8H_7NCl_2Br_2$. Calculated %: C 27.59; H 2.01; N 4.02.

2,6-Dichloro-3-(β-hydroxyethyl)-4-methylpyridine (V). A mixture of 360.9 g 2,6-dichloro-3-(β-acetoxyethyl)-4-methylpyridine and 1500 ml 2% alcoholic solution of hydrochloric acid was heated at the boil for 3 hours. The solution was then evaporated in vacuum and the residue distilled at 10 mm. B.p. 186-187°. Yield 296.8 g (98.9%) 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine. On cooling, the substance crystallized to form colorless crystals with m.p. 73-75°. * No depression of melting point in admixture with 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine.

2,6-Dichloro-3-(β-benzoylhydroxyethyl)-4-methylpyridine (VIII). A mixture of 10.3 g 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine, 50 ml anhydrous benzene and 7.1 ml benzoyl chloride was boiled for 2 hours. The cooled reaction mass was treated with 30 ml 6% sodium bicarbonate solution, and the benzene solution was separated and dried with potassium carbonate. After distillation of the solvent, the residue was distilled in vacuum at 8 mm to give 13.0 g (86.1%) 2,6-dichloro-3-(β-benzoylhydroxyethyl)-4-methylpyridine with b.p. 234-235°. The substance crystallized on standing. Recrystallization from anhydrous alcohol gave colorless crystals with m.p. 110°. The crystals are readily soluble in chloroform, soluble in benzene and acetone, poorly soluble in alcohol and ether, insoluble in water. The compound does not form a hydrochloride, picrate or methoiodide.

Found %: C 57.93, 57.81; H 4.36, 4.24; N 4.55, 4.82. $C_{15}H_{13}O_2NCl_2$. Calculated %: C 58.06; H 4.19; N 4.52.

6-Chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine (VII). A mixture of 8.0 g dry tert-amyl alcohol, 60 ml anhydrous toluene and 3.0 g metallic potassium was boiled while stirring for an hour. In the course of this period the potassium reacted completely. To the hot solution (110°) was added a solution of 10.3 g 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine in 150 ml anhydrous toluene. The reaction mass was stirred another 2 hours at room temperature and treated with 4.5 ml methyl iodide. After 12 hours, the precipitate of potassium iodide was filtered off and the filtrate evaporated in vacuum. The residual oil crystallized on standing. It was purified by distillation in vacuum. B.p. 167-169° at 10 mm. Yield 8.2 g (96.7%) 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine in the form of colorless crystals with m.p. 45.5-46°. The substance is readily soluble in ether, acetone, benzene, alcohol and chloroform, insoluble in water and ligroine; does not give a reaction for a double bond (with potassium permanganate and with bromine), does not contain a methoxy group.

Found %: C 56.87, 56.57; H 4.76, 4.99; N 8.13, 8.00; Cl 21.40, 21.16. C_8H_8ONCl. Calculated %: C 56.63; H 4.72; N 8.26; Cl 20.94.

The hydrochloride was obtained by saturating an ethereal solution of the base with dry gaseous hydrogen chloride. Colorless crystals with m.p. 98-98.5°, soluble in acetone, chloroform, methanol and ethanol, insoluble in ether and benzene. The hydrochloride is hydrolyzed by water.

4-Methyl-2,3-(2',3'-dihydrofurano)-pyridine (IX). To a solution of 9.3 g 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine in 150 ml ethyl alcohol was added a solution of 2.0 g palladium chloride ($PdCl_2$) in 11 ml 17% hydrochloric acid. The mixture was hydrogenated at room temperature under a pressure of 15-20 cm water column. The theoretical required amount of hydrogen (1.32 liters) was absorbed in the course of an hour. The catalyst was filtered off and the filtrate evaporated to dryness in vacuum. The hydrochloride of 4-methyl-2,3-(2',3'-dihydrofurano)-pyridine was recrystallized from a mixture of alcohol and ether. M.p. 141-142°. Yield 10.8 g (88.5%).

Found %: C 56.06, 55.79; H 5.91, 5.94; N 8.14; Cl 20.43, 20.43. $C_8H_9ON \cdot HCl$. Calculated %: C 55.98; H 5.83; N 8.16; Cl 20.69.

The free base forms colorless crystals with m.p. 53-54°, soluble in ether, acetone, benzene, chloroform and alcohol, poorly soluble in water and ligroine. B.p. 110.5-111° (7 mm).

* 2,6-Dichloro-3-(β-hydroxyethyl)-4-methylpyridine is reported to have b.p. 186-187° at 10 mm and m.p. 73.5-75° [1].

The picrolonate forms yellow crystals with m.p. 160-161° (with decomp.).

2-Chloro-3-(β-chloroethyl)-4-methylpyridine (X). A mixture of 4.3 g 4-methyl-2,3-(2',3'-dihydrofurano)-pyridine hydrochloride and 20 ml phosphorus oxychloride was heated in a sealed tube for 5 hours at 180-190°. The cooled reaction mixture was poured on to ice. The solution was neutralized with sodium carbonate and the separated oily substance was extracted with ether. The ether solution was dried with potassium carbonate, the ether distilled off, and the residue distilled in vacuum at 4 mm to give 3.55 g (77%) 2-chloro-3-(β-chloroethyl)-4-methylpyridine in the form of a colorless oil with b.p. 113-114°. The compound is readily soluble in organic solvents, insoluble in water; n_D^{20} 1.5533.

Hydrochloride – colorless crystals with m.p. 106.5-108°, soluble in water, alcohol, chloroform, poorly soluble in acetone and benzene, insoluble in ether and toluene.

Found %: C 42.48, 42.70; H 4.66, 4.81; N 5.87, 5.90. $C_8H_9NCl_2 \cdot HCl$. Calculated %: C 42.38; H 4.42; N 6.18.

2,6-Dichloro-3-(β-methoxyethyl)-4-methylpyridine (I). 1) 5.1 g metallic sodium was pulverized in anhydrous xylene, the xylene was poured off, and to the sodium (washed with anhydrous ether) was added a solution of 40.3 g 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine in 600 ml anhydrous ether. The reaction mixture was boiled and stirred for 60 hours and then cooled to 20°, treated with 10 ml methyl iodide and heated at the boil for another 10 hours. The sodium iodide was filtered off, the filtrate was evaporated in a vacuum on a boiling water bath, and the residue distilled in vacuum. Two fractions were collected: 1st with b.p. 154-189° at 10 mm, 31.5 g; 2nd with b.p. 250-270° at 5 mm, 4.0 g. The 2nd fraction, apparently a mixture of dipyridyls, was not investigated. The 1st fraction (an oily liquid) was a mixture of the original 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine, 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine and 6-chloro-2,3-(2',3'-dihydrofurano)-pyridine. The components were separated in the following manner: The oily liquid deposited crystals (7.4 g) on cooling; these were filtered and identified as 2,6-dichloro-4-methyl-3-(β-hydroxyethyl)-pyridine. For complete separation of the 2,6-dichloro-4-methyl-3-(β-hydroxyethyl)-pyridine dissolved in the products of the reaction, 24.1 g of the filtrate was boiled for 3 hours with 8.5 g benzoyl chloride and 50 ml anhydrous benzene. After cooling, the reaction mass was treated with 50% potassium carbonate solution and the separated alkaline solution was extracted with benzene. The combined benzene extracts were dried with potassium carbonate, the benzene was distilled off, and the residue distilled in vacuum at 5 mm. 22.5 g colorless oil was collected; b.p. 112-140°; this was a mixture of 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine and 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine. The higher boiling benzoin ether of 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine was not distilled. For separation of 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine, the solution of the oil obtained in anhydrous ether was saturated with dry gaseous hydrogen chloride. The precipitate (2.74 g) of the hydrochloride of 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine was filtered off and washed with ether. The filtrate was evaporated and the residue, consisting of 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine, was distilled in vacuum at 10 mm. B.p. 154-156°. Yield 17.6 g [40.7% reckoned on the 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine taken into the reaction]. A colorless liquid, readily soluble in organic solvents, insoluble in water. Does not form a hydrochloride, picrate, picrolonate or methoiodide.

n_D^{20} 1.5392, d_4^{20} 1.255, MR_D 55.42; calc. 55.47.

Found %: N 6.14; Cl 32.61; OCH_3 13.72. $C_9H_{11}ONCl_2$. Calculated %: N 6.36; Cl 32.27; OCH_3 14.09.

2) 85 ml dry tert-amyl alcohol, 10.1 g metallic sodium and 100 ml anhydrous toluene were stirred at the boil for 4 1/2 hours. To the cooled reaction mixture (20°) was added a solution of 70.0 g 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine in 150 ml anhydrous toluene. The reaction mass was stirred at room temperature for 9 hours, then treated with 35 ml methyl iodide, and the stirring continued another 12 hours. The precipitate of sodium iodide was filtered off, the filtrate evaporated on a water bath, and the residue distilled at 5 mm.

2 fractions were collected: 1st, b.p. 136-166°, 53.6 g; 2nd, b.p. 166-168°, 8.1 g.

The 2nd fraction was 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine (m.p. 73.5-75°).

The ethereal solution of the 1st fraction (a mixture of reaction products and a minute amount of starting substance) was saturated with dry, gaseous hydrogen chloride for the purpose of separation of 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine. The precipitate was filtered and dried in a vacuum desiccator. Yield 32.02 g (45.9%) of the hydrochloride of 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine (m.p. 98-98.5°). After precipitation of this hydrochloride, the ethereal solution was evaporated in vacuum, and the residue distilled at

10 mm. A fraction with b.p. 153-155° was collected; this was 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine. Yield 20.5 g (28%).

3) To a mixture of 50 ml anhydrous isopropyl alcohol and 50 ml anhydrous toluene was added 5.2 g metallic sodium. After the whole of the sodium had reacted, the reaction mass (cooled to −5°) was treated with a solution of 46.0 g 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine in 100 ml anhydrous toluene and stirred for 6 hours at the same temperature. 15 ml methyl iodide was then added and stirring continued at room temperature for another 12 hours.

The reaction mass was treated with 200 ml 25% NaOH solution and extracted with ether. The ethereal solution was dried with calcium chloride and saturated with dry, gaseous hydrogen chloride. The precipitate (0.9 g) of the hydrochloride of 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine was filtered off, the filtrate was evaporated in a vacuum, and the residue distilled at a residual pressure of 10 mm. Two fractions were collected: 1st with b.p. 154-157°, 35.7 g; 2nd with b.p. 184-187°, 8.8 g. The 2nd fraction was identified as 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine. The 1st fraction was 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine. Yield 71.6%.

3-(β-Methoxyethyl)-4-methylpyridine (II). To a solution of 4.35 g 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine in 100 ml alcohol was added a solution of 1.7 g palladium chloride in 15 ml 17% hydrochloric acid. The mixture was hydrogenated under a pressure of 40-50 cm water column at room temperature. Dehalogenation was completed in 12 hours. The catalyst was filtered off and the filtrate evaporated in vacuum. The resultant hydrochloride of 3-(β-methoxyethyl)-4-methylpyridine was treated with 60 ml 25% KOH solution, and the liberated base was extracted with chloroform. The chloroform solution was dried with potassium carbonate, the chloroform distilled off, and the residual 3-(β-methoxyethyl)-4-methylpyridine distilled in vacuum. B.p. 112-114° (12 mm). Yield 1.9 g (91.3%). Colorless, mobile oil, readily soluble in organic solvents, insoluble in water.

The hydrochloride was obtained by adding an alcoholic solution of hydrogen chloride to an ethereal solution of the base. It was recrystallized from a mixture of equal parts of benzene and acetone. Colorless, rectangular crystals with m.p. 118-119°, readily soluble in water, acetone, and alcohol, poorly soluble in benzene, toluene and chloroform, insoluble in ether.

Found %: C 57.40, 57.79; H 7.36, 7.41; N 7.33; Cl 18.65. $C_9H_{13}ON \cdot HCl$. Calculated %: C 57.60; H 7.47; N 7.47; Cl 18.93.

Methoiodide. The calculated amount of methyl iodide was added to an ethereal solution of the base. On standing for 12 hours, fine, colorless crystals of the methoiodide came down. M.p. 129.5-131°; on further heating the substance sublimes without decomposition.

SUMMARY

1. The synthesis of 3-(β-methoxyethyl)-4-methylpyridine was realized, starting from trichlorocollidine.

2. It was established that the chlorine atom in the β-chloroethyl group of trichlorocollidine enters with difficulty into substitution reactions but is readily split off in the form of hydrogen chloride with formation of a double bond.

3. A study was made of the conditions of formation of the alcoholate of 2,6-dichloro-3-(β-hydroxyethyl)-4-methylpyridine and of its transformation into 2,6-dichloro-3-(β-methoxyethyl)-4-methylpyridine and into 6-chloro-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine.

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